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THE PROBLEM OF SUPERGENE CASSITERITE IN BOLIVIAN TIN VEINS.[1]

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INTRODUCTION.

SINCE the general account of the Bolivian tin deposits with annotated bibliography was written in 1919 by Miller and Singewald, the economic importance of the Bolivian deposits has increased, foreign investments in their development have been greatly augmented, and they have attracted much attention on the part of geologists. Geologic literature treating of those deposits has had many additions, and knowledge of them has been greatly advanced. Articles contributing data relevant to the subject of this paper are listed in the bibliography at the end and are referred to in the text by their respective numbers. Of especial significance are the paragenetic studies of Davy, Hall, Lindgren, Buerger, Maury, and Creveling. The *Boletin Minero* established at Oruro in 1926 by E. Kittl is publishing many papers on the Bolivian mineral deposits.

A lively interest has been aroused in the subject of secondary tin enrichment in the Bolivian veins because of the paper by Koeberlin which appeared in 1926. A certain amount of corroborative evidence has been added, but no other observer has ascribed equal importance to secondary tin. Recent literature contains considerable negative evidence. The reader who has not carefully analyzed the data, weighed their significance, and tested the validity of the conclusions, is as much in the dark as to

[1] Presented before Society of Economic Geologists, New York Meeting, Dec. 29, 1928.

the rôle of supergene cassiterite as he was before the newer studies of the Bolivian veins.

An orderly analysis of the evidence bearing on the problem of supergene tin enrichment can be made by considering it under the four groups of criteria recognized by Ransome[2] in his discussion of the criteria of downward sulphide enrichment, namely (1) geological, (2) mineralogical, (3) chemical, and (4) textural.

STATEMENT OF PROBLEM.

A diminution of tin values with increasing distance from the outcrop, especially in the transition from oxidized ores to sulphide ores, is a long recognized and generally accepted phenomenon of the Bolivian tin veins. Very few detailed or comprehensive quantitative data as to the ratios of tin tenor in these ores have been assembled, and opinions on the amount of the change in tenor are largely subjective and inevitably influenced by preconceived ideas of the observer. The Bolivian veins are notable among the world's tin deposits because of the abundance and variety of stanniferous sulphides they contain. In the zone of oxidation these minerals are wanting. They have been oxidized and their tin content either carried away in solution or reformed as tin oxide. Wood tin has been considered a form of tin oxide of supergene origin, and the easy explanation was to consider it the product of the tin content of the sulphostannates. Cassiterite has been considered one of the most insoluble and resistant of minerals, and its solution and redeposition by descending waters have been conceded possible to a very limited extent only. From a quantitative standpoint, the tin content of the Bolivian ores, whether from the upper levels or the lower levels of the mines, lies in the mineral cassiterite. If the solution and redeposition of cassiterite on an important scale by meteoric waters does not take place, then supergene tin enrichment in the Bolivian veins can not be a process of much economic importance.

[2] F. L. Ransome: "Criteria of Downward Sulphide Enrichment." ECON. GEOL., vol. 5, pp. 205–220, 1910.

In 1915 and 1919, I had the opportunity of visiting most of the Bolivian tin districts, and my own observations accord with the conclusions set forth by Miller and Singewald in 1919 (*28*, pp. 101–2)[3] that tin enrichment in the zone of oxidation is primarily a process of residual enrichment involving the removal or reduction in amount of associated minerals and in special cases some mechanical transportation of cassiterite in that zone. Most of the oxidized tin ore is a very porous mass of cassiterite, quartz, and limonite. If the pore space were filled with sulphide instead of air, a much lower-grade tin ore would result. We stated that "the extent to which cassiterite is enriched by solution and redeposition in the zone of oxidation is a mooted question." In 1928 Ahlfeld, who agrees with Koeberlin to a greater extent than any one else who has discussed the subject, expressed a very similar opinion when he wrote (*2*, p. 44): "Concerning the chemical processes in the formation of secondary cassiterite we are today as ignorant as we are concerning the percentage it constitutes of the entire quantity of Bolivian cassiterite." Most writers have been extremely conservative as to the amount of solution and redeposition of cassiterite by supergene processes that they concede.

Koeberlin (19) has attributed great economic importance to the process of supergene tin enrichment in the Bolivian ores. He believes that the enrichment is not confined to the zone of oxidation but extends down into the sulphide ores. Residual enrichment he contends is inadequate to account for the amount of enrichment in the zone of oxidation, and of course does not apply at all to the sulphide ores. Koeberlin clearly recognized that large scale supergene tin enrichment involved repeated solution and redeposition of cassiterite to a commensurate extent, and that the difficulties of the problem could not be evaded by appealing to the stanniferous content of the sulphosalts, as they were wholly inadequate in amount, and because after the first cycle of solution further concentration depended on the solubility of the newly formed tin oxide. He frankly stated that no satisfactory chemi-

[3] Numbers in parentheses refer to bibliography at end of paper.

cal explanation of the process was known. The process itself is "solution of cassiterite in the upper parts of the vein; downward percolation; redeposition as tin oxide at lower levels." Koeberlin commits himself equally clearly as to the quantitative importance he attaches to the process in the statement (*21*, p. 820): "It is perhaps not too much to say that its economic significance with respect to tin lodes is almost as great as that of secondary sulphide enrichment in the case of copper deposits."

GEOLOGIC EVIDENCE.

Geologic evidence in support of supergene tin enrichment is presented by Koeberlin, Brown, Lewis, and Ahlfeld.

Koeberlin says many Bolivian tin mines have been worked only in the oxidized zone, the ores of which were often very rich. The grade of the sulphide ores was considerably lower, particularly in the smaller veins. Veins worked by successive adits down the hill side seldom yielded profitable ore when the adits entered the sulphides even though the vein showed no decrease in size. Pay ore seemed to be limited to a belt roughly parallel to the present surface. The San Fermin vein at Llallagua is described as having a barren oxidized zone and showing sudden enrichment with marcasite in the sulphide zone and a deep extension of the rich cassiterite and marcasite near a post mineral fault zone. The marcasite-cassiterite ore fades in depth to lower grade ore of uniform tenor without marcasite. More striking than the mineralogic changes in the San Fermin vein described by Koeberlin, is the coincidence of the rich ore, which consists of cassiterite, bismuthinite, and wolframite, with maximum vein width. This suggests that the rich ore occurs in primary ore shoots localized in the widest parts of the veins. Additional evidence cited by Koeberlin is that at Oruro high grade silver and tin ores diminished in tenor with increasing depth, the tin the more rapidly, so that in the lowest levels the ore is workable only as silver ore. In the Pazña district, at Totoral and Antequera, is a zone of oxidation with good values passing downward into low grade sulphides. The Totoral veins unite down the dip to form one

vein which in the sulphide zone becomes narrow and has low tin values associated with pyrite and sphalerite. The outcrops of the adjoining Avicaya veins run down the mountain side and the veins were workable over a much greater vertical range for that reason. At El Salvador, northwest of the Pazña district, the veins outcrop over a vertical range of 500 m., but good silver and tin values are not found much more than 50 m. below the outcrop. Below the tin ores are zinc ores with low silver and tin values. It is interpreted as a case of low grade zinc ore with an overlying secondarily enriched silver-tin zone. Potosi is mentioned as an important example of enrichment, but the evidence is not presented. At least some of the rich ore shoots at Potosi have been worked at depths greater than those to which supergene enrichment is likely to have reached. The Colorado Vein at Chocaya is cited as a case in which enrichment did not take place. Without naming the locality Koeberlin describes two parallel veins 300 m. apart with a dip of 60°. One of the veins without topographic expression has a filling of quartz, pyrite, siderite, and uniformly distributed cassiterite. The other vein, marked by a topographic depression, has had its vein structure destroyed by solution or crushing, or both, and the pyrite removed. The tin ore is finely crystalline, nearly amorphous oxide associated with disintegrated quartz, and lies in lenticles on the footwall side of the vein. He adds that the physical condition of the vein absolutely excludes the possibility of mechanical migration of the tin to the footwall, and regards the case as evidence of solution and redeposition of the tin.

Brown says in the Quimsa Cruz district are numerous small veins about 5 inches wide which contain extremely rich—up to 30 per cent. tin—sulphide ore within a few feet of the surface, but the high grade ore disappears within 10 to 20 feet along both strike and dip. He suggests that this ore may represent the remaining portion of an enriched zone. The description fits better an occurrence of small lenses and pockets of primary ore,—a characteristic phenomenon of narrow tin veins.

Lewis says wide experience in Australia and Tasmania has

brought to his attention many cases of pay ore in the outcrops succeeded by low grade ore in depth. Often the ore is richer than could be accounted for by the oxidation of pyrite and in some cases pyrite was never present. In other cases barren outcrops have rich oxidized ore beneath. These phenomena are cited as favoring secondary enrichment in Australia and Tasmania.

Ahlfeld says the high temperature veins carry mainly pure cassiterite and show no secondary enrichment, whereas the lower temperature veins carry cassiterite contaminated with iron and stannite, and show enrichment. Vila Apacheta at Chayanta is described as having an oxidized zone of 50 m. depth, a cementation zone from 50 m. to 160 m., and a primary zone that has been worked to a depth of 200 m. The vein shows leaching of stannite and deposition of wood tin. The Animas mine at Atocha is described as having an oxidized zone of 70 m. of rich *pacos* ores with compact secondary cassiterite and a little silver and an underlying zone of primary cassiterite, stannite, and pyrite with secondary silver ores that has been followed to a depth of 264 m. The Veta Colorado at Colcha has been developed to a depth of 250 m. A shallow oxidized zone contains a little cassiterite, and the underlying sulphide ore a little stannite. Encrusting siderite and pyrite on all levels are crystals of pure cassiterite which Ahlfeld suggests may have been deposited by descending solutions. After citing these specific instances of probable secondary cassiterite derived from stannite, Ahlfeld follows with the general statement that frequently a rich tin hat is succeeded by primary pyrite and sphalerite with a fraction of a per cent. of tin, and names Esmoraca, Tasna, and Porco as examples. He says these ores represent concentration of tin from a great overlying vein height. If copper is present, the tin was derived from stannite; in the absence of copper cassiterite must have been the source.

Spurr in editorial comment on Koeberlin's first article characterizes the evidence as impressive and says "one is impelled to respect his conclusions." Other statements in the editorial suggest that the comment is an acceptance of the conclusions.

Somewhat similar geologic evidence but differently interpreted is presented by Sznapka, Kozlowski, Jakowski, and Winkelmann. Sznapka discusses both primary and secondary differences in depth. As a primary difference in depth he cites an impoverishment in tin and silver and an increase in sphalerite with increasing depth. The diminution in the tin tenor in more rapid than that of silver. The increase in sphalerite with depth is especially marked in the tin vein type, as in the Quimsa Cruz region. In the discussion of secondary differences in depth, he says the *pacos* ores are richer in tin because of the removal of pyrite, and that the value of the oxidized ores is greater than that of sulphide ores of the same tin content because the latter have to be roasted.

Kozlowski also recognized a rapid decrease with depth in the tin content of the tin vein type, and a decrease in both silver and tin in the argentiferous stanniferous type. At Oruro veins that to a depth of 100 m. yielded ores with a tenor of 5 to 10 per cent. tin, at 300 to 400 m. carried 1 to 2 per cent. or less tin. Tin tenor dropped more rapidly than did the silver. The first mineral to form was pyrite, and in depth the pyrite filling of the veins is more compact. Potosi is described as exhibiting the same phenomena. Kozlowski considers these primary changes in depth and not due to supergene processes.

Jackowski recognizes an unequal downward distribution of the tin content of the Bolivian veins but refers the change to primary causes. He suggests a rapid change in the amount of tin deposited in the transitional zone from gaseous to liquid state of the ascending mineralizers in which zone a medium grade vein might suddenly become very rich and then terminate above in a barren zone.

Winkelmann, studying a suite of ores collected by the late Professor Scheibe, recognized enrichment of cassiterite in the oxidized zone but says it is analogous to the formation of eluvial placers. The cassiterite was not attacked by the oxidation.

Scrivenor in a discussion of Koeberlin's article says that in the Malay States there is no evidence of solution and redeposition of cassiterite. Kittl (*16*, p. 187), who has a wide knowledge of the

Bolivian tin deposits, criticises Ahlfeld for taking up the "little proven and much exaggerated" ideas of Koeberlin. He says he has carefully studied the question and finds secondary cassiterite not nearly so abundant as claimed, but considers it is an advance to point out that all cassiterite is not primary.

Dr. Robert M. Overbeck, who has had more experience in the careful examination of Bolivian tin mines than any other geologist, tells me he has seen no evidence of secondary enrichment being of economic importance.

The geologic evidence cited above establishes the occurrence of rich oxidized tin ores in the Bolivian veins underlain by leaner sulphide ores characterized by further diminution of tin content wth increasing depth. Supergene cassiterite deposition is not a necessary conclusion from these facts. So far as the tenor of the oxidized ores is concerned it is a matter of personal opinion whether it can be adequately accounted for or not by processes of superficial alteration in the zone of oxidation that do not involve considerable solution and redeposition of cassiterite. Decrease in the content of a valuable metal in sulphide ore with increasing depth may be a phenomenon of primary mineralization and is not necessarily the indication of a fading zone of cementation.

In evaluating the significance of the foregoing geologic evidence, it is necessary to keep in mind the paucity of quantitative data and the irregularity in the distribution of the tin content of the primary mineralization itself. Information concerning relative tenors of ores from the zone of oxidation and from the underlying sulphidic ores is so general that it is not possible to separate the residual enrichment in the zone of oxidation due to the oxidation and leaching of sulphides and other more readily soluble constituents of the ore from such enrichment as may be due to solution and redeposition of cassiterite, and thus actually determine the quantitative importance of the latter. The veins that carry profitable primary ores and have been worked to greater depths are characterized by variations in tenor laterally and vertically and by the occurrence of the mineable ore in ore shoots of restricted extent. Careaga (*6*, p. 199) describes a marked

variation in primary metallic content with increasing depth in the Veta Colorado at Chocaya. The 12th level ore was richer than that of the 11th level, an impoverishment followed to the 14th level, and the 15th level was again as rich as the 12th level. This variation is said to show a close relation to the physical character of the fissure. Where the vein is wide and well formed, or at junctions with the closely paralleling Llampera vein, the ore is rich. Where the vein splits up into stringers, the ore is lean. The vicissitudes of the Caracoles mine in the Quimsa Cruz region exemplify this condition in a very striking way. If those veins were not worked by a company with adequate financial resources to push through barren vein areas, they would have been abandoned long since, because repeatedly known ore shoots have terminated and only barren ground lay ahead. This feature of the veins would explain in part the shallow depth of so many of the Bolivian tin mines. Among the many outcrops of veins, those veins are chosen for exploitation that show an outcrop of workable ore. Such an outcrop represents an outcropping ore shoot. Within limited vertical depth, the ore shoot is passed through and unworkable leaner material is encountered below. The vast majority of Bolivian tin mines have been worked in primitive fashion with very limited capital. The operators have not had the equipment nor the means to conduct systematic prospecting through barren areas to find out what lay beyond or below an ore shoot. Consequently when an ore shoot was exhausted, many mines were abandoned and other outcropping ore shoots were sought. This condition would falsely suggest a relation between present surface and rich ore. To prove or disprove such a relationship requires more information than has been presented or is available. Stope sheets showing the size and distribution of ore shoots in the oxidized and primary zone and the tenor of ore and total metallic content of the shoots alone can furnish determinative data for the solution of this problem. Very few of the Bolivian tin veins have been extensively enough worked to be capable of supplying such data. In the case of only a few veins have such data been assembled.

So far as I know such information has not been available to those who have discussed the distribution of the tin content of the Bolivian veins.

The geologic evidence of supergene cassiterite enrichment is not adequate to prove that it played an important part in the formation of the workable tin ores. It can not be rated as doing more than supporting the possibility of its effectiveness and suggesting the desirability of closer consideration of other possible lines of evidence.

MINERALOGICAL EVIDENCE.

The tin-bearing minerals of the Bolivian tin veins are cassiterite, wood tin, and the sulphostannates. None of these minerals are exclusively of supergene origin, so that there are no tin minerals which are unequivocal evidence of downward enrichment.

Though a supergene origin has been ascribed to the sulphostannates, it will be shown in the discussion of the textural evidence that there is almost unanimity of opinion in referring these minerals to the hypogene mineralization. Furthermore, as Koeberlin himself has pointed out more than once, the rôle of the sulphostannates is a subordinate one and the problem of downward enrichment involves the oxide of tin and not the sulphosalts. The statement of Ahlfeld (*1*, p. 82) that Oruro primary stannite is always massive and intimately intergrown with other minerals and that the secondary stannite is pure and crystallized, even though accepted, has no practical bearing on the problem. Davy (*8*, p. 475) says there is no evidence of supergene tin sulphides unless an unknown supergene mineral which he observed be a tin mineral. Greene (*10*, p. 417) speaks of a secondary tin mineral in the oxidized zone at Llallagua but gives no description of it. Koeberlin (*19*, p. 640; *21*, p. 820) thinks the sulphostannates at Llallagua are secondary because marcasite is interlaminated with franckeite and associated with greenockite.

There has been a tendency to regard wood tin as of secondary origin formed by descending solutions, but many instances are now on record of its deposition by hypogene solutions. The

fairly abundant occurrence of wood tin in Boliva is consequently not necessarily evidence of supergene deposition, and there is considerable evidence to show that some of it was deposited by ascending solutions. Ahlfeld (*1*, p. 82) says through decomposition of stannite, porous cassiterite or banded masses of wood tin can result. Davy (*8*, p. 475) thinks the oxidized character of the material associated with wood tin suggests its supergene origin and derivation from stannite. He finds that it has probably replaced both crystalline quartz and cassiterite, two minerals notably insoluble in acid solutions. Hence he presents the difficulty that a pronounced change from acidity to alkalinity in the supergene tin-bearing solutions would have to be accounted for. Gruner and Lin suggest the slow solution of stannite as the source of the tin deposited in lower levels as wood tin. Kittl (*15*, p. 50) considers the iron hydroxide content of wood tin as evidence of secondary origin and believes it is formed in the zone of oxidation. Again (*17*, p. 267) he refers to its association with marcasite as evidence of its secondary origin. Whether cassiterite or wood tin is formed he thinks depends on the composition and temperature of the depositing waters.

It is not necessary to cite many examples of wood tin of hypogene origin from other regions. A notable example is that described by Knopf [4] in Nevada. Collins [5] has described wood tin from Durango with crystals of cassiterite on it and in cracks in it together with quartz, tourmaline, and chlorite. Their significance is that wood tin may be of hypogene origin and its presence in an ore cannot be accepted as proof of supergene transportation of tin oxide.

The only possibility of distinguishing between primary and secondary cassiterite would be because of differences in crystal form or other physical properties. Ahlfeld and Greene consider needle tin of supergene origin. Ahlfeld (*1*, p. 82) regards needle tin evidence of secondary deposition from primary stan-

[4] Knopf, Adolph, "Wood Tin in the Tertiary Rhyolites of Northern Nevada," ECON. GEOL., vol. 11, pp. 652–661, 1916.

[5] Collins, J. H., "Additional Notes on Wood Tin," *Mineralogical Magazine*, vol. 16, pp. 30–34, 1910.

nite or other sulphostannates. Greene speaks of needle or honey tin occurring generally on wurtzite and of secondary origin. The needle tin at Monserrat coats the other vein minerals and seems to be the last in the paragenetic sequence. But it is not associated with supergene minerals and is probably of late hypogene deposition. Winkelmann (*35*, p. 107) describes needle tin at Uncia in pneumatolytically altered rhyolite in tourmaline zones and in cleavage planes of colorless mica. This must be of hypogene origin. Kittl and Koeberlin recognize secondary cassiterite because of associated minerals. Kittl (*15*, p. 50) describes cassiterite from Huanuni associated with limonite and natrojarosite but concedes that the cassiterite may be the remains of an earlier pyrite-cassiterite ore. Koeberlin (*19*, p. 640) cites the association of marcasite with cassiterite in the rich ore shoot of the San Fermin vein at Uncia with a limited downward extension. Since marcasite is a low temperature mineral, he does not consider the associated cassiterite primary. This is a rather dubious inference.

One is forced to the conclusion that there are no tin-bearing minerals in the Bolivian veins whose mere presence is evidence of secondary tin enrichment. Mineralogic criteria can not be marshalled in support of important secondary tin enrichment in these veins.

CHEMICAL EVIDENCE.

It has already been pointed out that if supergene tin enrichment played an important rôle in the Bolivian tin veins the process involved mainly the solution, transportation and redeposition of cassiterite. Let us test the probability of the effectiveness of such a process in the light of knowledge concerning the solubility of cassiterite.

The outstanding characteristic of cassiterite under usual conditions of rock decay and weathering is its insolubility and resistance to those influences. This is attested by the fact that over half of the world's tin production consists of placer cassiterite. Those constituents of ore deposits and rocks accumulate in placers that resist solution. This is very strong *a priori* evidence against

the occurrence of supergene cassiterite on a large scale. It must be recognized, however, that minerals which resist solution under certain conditions may succumb under other more favorable conditions. A very striking example of such a difference is cited by W. H. Emmons [6] in the case of gold. Gold is very resistant to solution and easily reprecipitated so that under ordinary conditions in veins it migrates with great difficulty. The consequence is that outcrops of gold veins are commonly removed by erosion more rapidly than the gold moves downward, and the gold accumulates in placers. Emmons found that manganese in the vein filling facilitates solution and retards reprecipitation, thereby making possible a more extensive downward migration of the gold. In such veins the descent of the gold may be more rapid than the denudation of the outcrop. No placers will be formed and the veins will be characterized by supergene gold enrichment. This marked difference in behavior of gold in two neighboring mines is illustrated by the Cable and Granite-Bimetallic mines in the Phillipsburg, District, Montana. A somewhat analogous case for silver has been described by Earl V. Shannon [7] in the Coeur d'Alene District, Idaho. The Caledonia mine shows a markedly greater silver enrichment than adjoining mines. Its vein filling differs in a greater abundance of the favorable mineral chalcopyrite which affords the solvent iron sulphate and less of the unfavorable mineral siderite which occurs so abundantly in the Coeur d'Alene veins. Although cassiterite is not taken into solution in most tin deposits, may there not be some peculiarly favorable conditions in the Bolivian tin veins which make possible supergene enrichment? The many departures of the Bolivian deposits from the normal or typical tin vien type, as established by the earlier studies of the European tin districts, lend a certain probability to such a possibility.

W. H. Emmons (*9*, p. 399), Gruner and Lin, J. B. Scrivenor,

[6] Emmons, W. H., "The Agency of Manganese in the Superficial Alteration and Secondary Enrichment of Gold Deposits in the United State," *Trans. Amer. Inst. Min. Engrs.*, vol. 42, p. 58, 1912.

[7] Shannon, Earl V., "Secondary Enrichment in the Caledonia Mine, Coeur d'Alene District, Idaho," ECON. GEOL., vol. 8, pp. 565–570, 1913.

E. Kittl (*18*, p. 106) and Careaga (*6*, p. 199) do not place much credence in the solubility of cassiterite under supergene conditions. Emmons says Frank L. Hess informs him that cassiterite from tin deposits in widely separated parts of the world is rarely much corroded and adds the statement that neither stannous nor stannic chloride or sulphate are stable in the ordinary oxygenated waters of the upper zone of ore deposits. Gruner and Lin describe two-month solution tests on both cassiterite and stannite. Cassiterite showed practically no solubility in cold dilute acid solutions. A limited solubility of stannite suggested the possibility of the transportation of colloidal tin, the dehydration of which would give rise to wood tin. Scrivenor says there is no evidence in British Malaya of the solution and redeposition of cassiterite. An experiment which he conducted for over a year on finely powdered cassiterite gave no evidence of solubility. Kittl, combating the rôle of phosphoric acid as a solvent, which was advocated by Greene, says the influence of phosphoric acid is not great and could be only local, so that sulphuric acid must play the main rôle. If this reagent were capable of dissolving and transporting cassiterite, corroded cassiterite ought to be encountered frequently. Despite the presence of limonite, sulphates, etc., evidencing complete decomposition of sulphides, cassiterite, he says, is generally encountered with brilliant faces and without indication of corrosion. Careaga finds that in the Veta Colorada at Chocaya there is evidence of secondary alterations, but that the cassiterite has not been affected.

Evidence of varying weight in support of supergene cassiterite is advanced by J. H. Collins, M. W. Davy (*8*, p. 475), F. R. Koeberlin (*20*, p. 503), G. U. Greene, P. A. Wagner, and H. Winkelmann (*35*, p. 107). The possible presence of stanniferous solutions is indicated by Collins' statement that wood tin is sometimes soluble to a remarkable degree in hydrochloric acid. However, the solubility of wood tin does not explain supergene cassiterite. Davy found that the solutions which deposited wood tin dissolved quartz and cassiterite, two minerals notably insoluble in acid solutions. He concludes: "therefore, any ex-

planation must account for a pronounced change from acidity to alkalinity in the tin-bearing solutions." This leaves the source and character of the solutions which dissolved the cassiterite in doubt, and its solution is established only in connection with the deposition of wood tin. Koeberlin cites a personal communication from E. H. Davison that bones dug up at the bottom of some alluvial gravels had the bony tissue partly replaced by cassiterite. Against Gruner and Lin's objection that only a very powerful reducing agent like hydrogen could make possible the solution of tin oxide in an acid solution, he says cassiterite in close association with pyrite undergoing oxidation is not itself under oxidizing conditions. Wagner, discussing Koeberlin's theory, cites the replacement of earlier quartz by cassiterite and its replacement in turn by silica gel in the Potgietersrust pipes. Corrosion of cassiterite by chalcedony and quartz is shown at this locality. But he ascribes the action to a late hydrothermal or low temperature stage not much above and possibly lower than 100° C. It is consequently a hypogene and not supergene process. Winkelmann describes the corrosion and replacement of cassiterite by quartz at Monte Blanco, but likewise ascribes it to a late thermal phase. The strongest evidence is that presented by Greene. He concedes the difficult solubility of pure cassiterite in acid solutions, but suggests that the iron oxide in an impure cassiterite like that at Llallagua, which contains only 94.06 per cent. SnO_2 and 4.30 per cent. iron, would set up a difference in potential which might be a controlling influence in facilitating solution. On the other hand, Boydell, who attacks the problem from the standpoint of physical chemical theory, doubts if impurities increase solubility. Greene found, however, that three samples of Llallagua mine water contained 19.4 to 180.9 mg. tin per liter, proving some solution of tin by meteoric waters in that mine. Greene did not prove, however, that the tin represented dissolved cassiterite. It is not improbable that its source was oxidizing stannite. Solubility experiments which he conducted indicated phosphoric acid to be the best acid solvent, and he says the Llallagua ores contain the phosphates vivianite, wavellite, vauxite, and paravauxite.

Koeberlin (*19*, p. 639; *21*, p. 820; *22*, p. 282), Spurr, and Boydell argue for the probability of cassiterite solution by supergene waters from the standpoint of physical chemical theory. The basis of these arguments is the impure nature of the Bolivian cassiterite and its association with minerals not characteristic of tin deposits in those districts which do not furnish evidence of solution and redeposition of cassiterite. Koeberlin makes little attempt to explain the chemistry of the process. He rightly says geologic facts must be accepted even though their chemical explanation is not yet forthcoming. As purely speculative, he suggests the presence of pyrite may exercise a reducing action facilitating solution as lower valence compounds or the presence of copper minerals may bring about a transitional stannite alignment. He also points to the impurity of Bolivian cassiterite as compared with that from Saxony and the Straits Settlements as a possible factor favoring secondary enrichment. Greene, he says, shows enough solubility of tin, with the time available, to dissolve and reprecipitate the largest Bolivian ore bodies several times over. Spurr sees considerable plausibility in Koeberlin's theory. He says the stability of minerals in ground waters depends to a degree not yet evaluated upon the associated minerals and that solubility may be due to chemical or electrochemical reactions caused by the complexity of the Bolivian ores. On the other hand, Boydell states that the available electrochemical data indicate decreased solubility for both heterogeneous impure cassiterite and impure homogeneous cassiterite. But on general principles he believes cassiterite must have some solubility in water at ordinary temperatures. Because of chemical similarities in tin oxide and silica he believes the solutions to be true and colloidal, and that stable tin oxide sols may have migrated considerable distances. The occurrence of wood tin suggests to him a colloidal stage in the history of cassiterite. Boydell concludes that, meager though the evidence is, it is sufficient to suggest variation in the solubility of cassiterite, conditions for its solution not being fulfilled in the case of some veins.

The foregoing data and discussions of the chemical evidence of

supergene cassiterite demonstrate the need of caution in utilizing the preponderant evidence against solution and reprecipitation of cassiterite as the basis for a denial of its possibility. There is positive evidence of the solution of cassiterite and of the presence of an appreciable quantity of tin in supergene mine waters. But much of the solution has been effected by hypogene waters; and the evidence of tin in supergene waters rests on the single case of Llallagua. Various physical chemical phenomena suggest the possibility of solution when conditions are peculiarly favorable. The advocates of supergene cassiterite *believe* the Bolivian veins present such conditions. But one is forced to the conclusion that the chemical evidence permits neither the categorical denial of the possibility of supergene cassiterite nor the assertion that there is clear chemical evidence of the operation of such a process. In other words, available chemical evidence does not make out a conclusive case either for or against the deposition of supergene cassiterite.

TEXTURAL EVIDENCE (PARAGENESIS).

The strongest evidence that could be marshalled in support of supergene cassiterite would come out of the paragenetic relations of the ore minerals in the vein filling. The advocates of enrichment have completely overlooked this line of evidence. Since the summary of existing knowledge concerning the Bolivian tin veins was written by Miller and Singewald in 1919, important additions have been largely in the form of paragenetic studies of the ores. If there has been much enrichment in cassiterite by supergene processes, the paragenesis of the ores should clearly show two generations of cassiterite, the younger of which should be later than the youngest of the hypogene minerals. The paragenetic studies have been made by workers not influenced by a desire to prove or disprove supergene cassiterite. Their observations and deductions should be entirely objective and hence worthy of acceptance as correct.

The importance of microscopic studies of the ores in the consideration of this problem was recognized by a number of those who have discussed Koeberlin's papers. As early as 1923,

Sznapka wrote that microscopic studies were desirable in order to determine the paragenesis of the ore minerals and to answer the questions whether and to what depths secondary enrichment occurred. Strauss criticised Koeberlin for failing to back up his redeposition suggestion with petrographic evidence. Though inclined to accept Koeberlin's views in part, Ahlfeld (*1*, p. 81) lamented the lack of a microscope, which he recognized as necessary for a satisfactory attack of the problem. After arguing rather favorably to Koeberlin from the standpoint of physical chemical theory, Boydell concludes that "the really essential point is to establish the definite deposition, in the absence of stannite from the ore, of cassiterite (or wood tin) on later minerals of the paragenetic sequence, such as the sulphides and silver minerals." I do not see the need of requiring the absence of stannite and would rephrase the criterion to read "the really essential point is to establish the deposition of cassiterite (in considerable quantity) on later minerals of the paragenetic sequence (those minerals being the sulphides and silver minerals)." Let us examine the evidence on that point.

Greene presents evidence of cassiterite definitely younger than a sulphide. He found a vug with loose crystals of bismuthinite completely coated with crystalline cassiterite which he regarded as evidence of deposition from solution and that the cassiterite is undoubtedly secondary. The cassiterite is obviously younger than the bismuthinite in that vug. But bismuthinite and cassiterite overlap in the hypogene paragenetic sequence so that some cassiterite is later than some bismuthinite. The sequence alone can not be interpreted as proving the cassiterite supergene.

Kozlowski, and Buerger and Maury describe repeated successions of cassiterite and sulphides. Kozlowski mentions among the principal characteristics of the Oruro deposits the contemporaneous formation of the tin ore and silver, the abundance of metallic sulphides, and the frequent occurrence of tin sulphide. In the Potosi ores he says bands of compact cassiterite alternate with bands of stannite, tetrahedrite, and pyrite. Buerger and Maury give as the sequence of the Chocaya ores pyrite, quartz

and cassiterite succeeded by stannite replaced by sphalerite and galena, then tetrahedrite, and finally jamesonite. Oft-repeated cycles of this sequence gave rise to cockade and banded ores. These phenomena are explained as due to repeated refreshing of the mineralizing solutions. They establish the hypogene origin of all of the minerals involved.

More adverse to supergene cassiterite are the other paragenetic studies. Davy, studying an extensive suite of Bolivian ores, arrived at the general sequence: quartz and cassiterite; sulphostannates; stannite, sphalerite, and chalcopyrite; tetrahedrite; and jamesonite. All of these minerals were considered hypogene. Hall examined my own collections from most of the important Bolivian tin districts and likewise placed the cassiterite earlier than the argentiferous sulphantimonides. Lindgren (*25*, p. 227) put the cassiterite of the Chacaltaya ores in the early hypogene mineralization and older than stannite, fluorite, and pyrite. In the Caracoles ores (*26*, p. 138) he places cassiterite earlier in the paragenetic sequence than pyrite, sphalerite, and bismuthinite. At Potosi, Lindgren and Creveling give as the sequence from early to late primary minerals pyrite, cassiterite, stannite, sulphantimonides. They recognize as supergene minerals chalcopyrite, ruby silver, chalcocite, and covellite, without mention of cassiterite. Winkelmann says the sulphides fall into two groups —one immediately following cassiterite including arsenopyrite, pyrite, and marcasite, and a younger group of sphalerite, galena, and chalcopyrite. In other words, he recognizes cassiterite only as older than undoubted primary sulphides. Kittl (*18*, p. 108) states that no cassiterite younger than stannite has yet been observed. Careaga (*6*, p. 201) recognizes cassiterite only as an early hydrothermal mineral preceding the hydrothermal silver minerals.

It would seem certain that if secondary cassiterite were an important feature of the Bolivian tin veins, it would not have escaped detection in all of these microscopic investigations of the paragenetic sequences of the minerals. The unanimity of interpretation in ascribing the cassiterite to the early stage of the hy-

pogene mineralization is imposing evidence against any theory postulating important supergene cassiterite enrichment in the Bolivian veins which involves the solution and redeposition of cassiterite. It becomes incumbent upon the advocates of such a process to present equally conclusive evidence of cassiterite younger than the late hypogene sulphides before they can consider their theory established.

CONCLUSION.

It has been shown that the geologic evidence in support of supergene cassiterite enrichment in the Bolivian tin veins is meager and by no means conclusive. Definite mineralogic evidence is wholly lacking. There is no convincing chemical evidence establishing a high degree of probability for such a process. Satisfying evidence would have to include proof of the occurrence of cassiterite younger in the paragenetic sequence of the vein-forming minerals than the late hypogene sulphides. The proponents of the theory have entirely neglected this most important line of evidence. Numerous paragenetic studies of the Bolivian tin ores are unanimous in placing cassiterite early in the sequence and older than the late sulphides of the hypogene mineralization. The available evidence does not warrant the conclusion that the Bolivian tin veins present the unusual phenomenon of important supergene cassiterite enrichment.

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SOLUTION, TRANSPORTATION AND PRECIPITATION OF IRON AND SILICA.

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PART II.

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PRECIPITATION OF IRON.

Precipitation of Ferric Oxide Hydrosols by Electrolytes.—Considerable work has been done on the precipitation of colloidal ferric oxide by electrolytes such as exist in sea water but in every case the concentrations of the hydrosols were far greater than occur in nature, assuming that all the iron carried by rivers is in the colloidal form. According to Clark [58] the average iron content of the rivers of the world calculated as $(Fe.Al)_2O_3$ is only 4.76 per cent. of the total mineral content.

In 1900 Hardy [59] did some quantitative work on the precipitation of ferric oxide hydrosols by electrolytes. He found that

[58] Clark, *op. cit.*, p. 119.

[59] Hardy, W. B., *Proc. Roy. Soc.*, 66, pp. 95 and 116, 1900.

one gram-molecule of magnesium sulphate, potassium sulphate, or sodium sulphate in 100,000 c.c. of solution was sufficient to coagulate the sol immediately. Sodium chloride had no effect. In other words, he found that 1200 parts per million magnesium sulphate, 1,742 parts per million potassium sulphate, and 1,420 parts per million sodium sulphate were sufficient to precipitate the ferric oxide hydrosol, but that 584 parts per million sodium chloride was insufficient to cause precipitation. Hardy found, also, that one gram-molecule of magnesium sulphate or one gram-molecule of potassium sulphate precipitated the ferric oxide from 4,000,000 c.c. of hydrosol. One gram-molecule of sodium chloride caused precipitation from 20,000 c.c.[60] A recalculation of values shows that 43.5 parts per million potassium sulphate or 30 parts per million magnesium sulphate coagulated the sol, while 1949 parts per million sodium chloride were required to produce the same effect. Hardy makes no mention of the concentration of the ferric oxide sols that were used.

Picton and Linder[61] carried out a series of experiments on the precipitation of ferric oxide hydrosols. They make no mention of the concentration of the sol. They conclude that the hydrosol is precipitated by the negative anions, and that dibasic acids and hydroxides are 240 times as effective as monobasic acids and hydroxides.

Freundlich[62] found that a colloidal iron sol containing 0.823 grams per litre Fe_2O_3 was flocculated by 9.25 millimols of sodium chloride, 0.205 millimols of potassium sulphate, or 0.22 millimols of magnesium sulphate. A recalculation of values shows that a colloidal solution containing 823 parts per million ferric oxide requires 536 parts per million sodium chloride, 356 parts per million potassium sulphate, or 26.4 parts per million magnesium sulphate to flocculate the iron. Later, Freundlich[63] performed another series of experiments on the precipitation of ferric oxide

[60] *Idem*, p. 117.

[61] Picton, H., and Linder, S. E., *Jour. Chem. Soc.*, 87, pp. 1926–1931, 1905.

[62] Freundlich, H., *Zeit. f. Phys. Chem.* 44, p. 151, 1903; "Colloid and Capillary Chemistry," p. 421, 1926.

[63] Freundlich, H., *Zeit. f. Phys. Chem.*, 73, p. 387, 1910.

hydrosols. He found that a ferric oxide hydrosol containing 1.744 grams of $Fe(OH)_3$ per litre was precipitated by 9.03 millimols of potassium chloride, 11.9 millimols of potassium nitrate, 9.25 millimols of sodium chloride, 0.217 millimols of magnesium sulphate, or 0.204 millimols of potassium sulphate. Recalculation of values shows that a ferric oxide hydrosol containing 1302 parts per million ferric oxide required 670 parts per million potassium chloride, 1,203 parts per million potassium nitrate, 536 parts per million sodium chloride, 26 parts per million magnesium sulphate or 35.5 parts per million potassium sulphate to precipitate the iron.

Duclaux [64] working with various kinds of ferric oxide hydrosols found that equal quantities of the hydrosols containing 0.0203 gram-atoms of iron per litre, which equals 1,620 parts per million ferric oxide, were precipitated by almost equivalent quantities of anions, such as sulphate, carbonate and hydroxide, regardless of the valency. He found, however, that the Schulze-Hardy precipitation law did not hold for the nitrate ion or for sodium chloride, exceptionally high concentration of these being required for precipitation. Recently Weiser and Middleton,[65] and Sen, Canguly and Dhar,[66] did some work on the precipitation of ferric oxide hydrosols. Weiser and Middleton, using ferric oxide hydrosols containing 1.544 grams of iron oxide per litre, found that 0.437 milli equivalents of potassium sulphate, 103.1 of potassium chloride or 131.2 of potassium nitrate caused complete coagulation of the iron. A recalculation of these values shows that a ferric oxide hydrosol containing 1544 parts per million ferric oxide is coagulated by 39 parts per million potassium sulphate, 6,027 parts per million potassium chloride, or 13,264 parts per million potassium nitrate. These results show that a great deal more than equivalent quantities of precipitating ions are required for coagulation in a number of cases. They

[64] Duclaux, J., *Jour. de Chim. Phys.*, 36, 1907.

[65] Weiser, H. B., and Middleton, E. B., *Jour. Phys. Chem.*, 24, pp. 30 and 630, 1920.

[66] Sen, K. C., Canguly, P. B., and Dhar, P. B., *Jour. Phys. Chem.*, 28, pp. 316–318, 1924.

explain this increase in the quantity of precipitating ions by assuming the adsorption of the electrically neutral particles during the process of agglomeration and settling of the hydrosol as well as the adsorption of the electrically charged particles during the process of neutralization.

Sen, Canguly and Dhar, did important work on the precipitation of ferric oxide hydrosols, for they worked with negative as well as with positive sols. Previous to the time this work was done, the experiments on the precipitation of ferric oxide hydrosols by electrolytes had been carried out only with positive sols. These authors found that 5 c.c. of a negative ferric oxide hydrosol containing 0.22725 grams of ferric oxide per litre was precipitated by 0.485 c.c. of $N/10$ KCl, 0.41 c.c. of $N/5$ NaCl, 0.249 c.c. of $N/10$ K_2SO_4 or 0.39 c.c. of N.NaOH. In other words a negative ferric oxide hydrosol containing 227 parts per million ferric oxide was precipitated by 659 parts per million KCl, 886 parts per million NaCl, 320 parts per million K_2SO_4, or 2894 parts per million NaOH. They reconducted the experiments with negative ferric oxide sols containing 454 and 909 parts per million ferric oxide, and found that the greater the concentration of the sol the greater the concentration of electrolytes necessary for coagulation, irrespective of the valency of the precipitating ions. They obtained similar results in their experiments with positive ferric oxide sols. They found, for example, that 0.8 c.c. of $N/200$ $MgSO_4$ flocculated 5 c.c. of positive ferric oxide hydrosol containing 0.25 grams of ferric oxide per litre, that 0.6 c.c. of $N/200$ $MgSO_4$ flocculated 5 c.c. of positive ferric oxide hydrosol containing 0.05 grams of ferric oxide per litre, and that 0.65 c.c. of $N/200$ $MgSO_4$ flocculated 5 c.c. of positive ferric oxide hydrosol containing 1.000 parts per million ferric oxide. A recalculation of these results shows that positive ferric oxide hydrosols containing 250 parts per million ferric oxide, 50 parts per million ferric oxide, and 1,000 parts per million ferric oxide, were precipitated by 41 parts per million $MgSO_4$, 32 parts per million $MgSO_4$, 34.5 parts per million $MgSO_4$.

The above experiments indicate that positive and negative ferric

oxide hydrosols varying from 50 to 1,000 parts per million ferric oxide are precipitated by electrolytes, the concentrations of which vary from 24 to 13,000 parts per million. The precipitating power depends on the electrolyte and on its valency. There is considerable disagreement among the various investigators as to whether equivalent quantities of the various ions cause precipitation of equal quantities of the ferric oxide hydrosols and as to whether greater dilution of the hydrosols necessitates greater or less concentration of the precipitating ions. This discussion is of little importance geologically, for even the most highly concentrated ferric oxide hydrosol is precipitated by a concentration of electrolyte far below the electrolyte concentration of the ocean the mean of which is about 34,400 parts per million.

The results given above indicate that all the iron carried to the ocean by streams is precipitated almost immediately by the electrolytes of the ocean providing the iron is in the colloidal form. In order to make certain of this point, a few experiments were performed on the precipitation of ferric oxide hydrosols by electrolytes such as are in the ocean, and ferric oxide hydrosols were used in concentrations more in accord with those that occur in nature. The average iron content of the rivers of the world, as mentioned previously, is only 4.76 per cent. of the total mineral content.

The first type of ferric oxide hydrosol was made by a method given by Holmes,[67] A concentrated solution of ferric chloride was poured into 600 c.c. of boiling water, the liquid was then allowed to cool, after which it was filtered and dialyzed through collodin membranes until free from chloride ions, as indicated by a silver nitrate test. The colloidal solution thus prepared was analysed and then so diluted that it contained 10 parts per million ferric oxide.

To 50-c.c. samples of the ferric oxide hydrosol containing 10 parts per million ferric oxide were added the following powdered salts in the proportion of 34,400 parts per million: sodium chloride, potassium chloride, potassium sulphate, potassium nitrate,

[67] Holmes, H. N., "Laboratory Manual of Colloid Chemistry," 1922.

magnesium sulphate, sodium hydroxide, and sea salt (salt obtained by the evaporation of sea water). A precipitate of ferric hydroxide, in every case, formed at once. Each solution at the end of two weeks was filtered in order to determine whether complete coagulation of the ferric oxide hydrosol had taken place, and the filtrate was tested for iron in the following manner; a small quantity was acidified with strong hydrochloric acid, boiled, evaporated to small bulk, and tested for ferric iron by potassium ferrocyanide. There was no indication of prussian blue in all the tests carried out, showing that complete coagulation of the hydrosols had taken place.

Experiments were conducted, also, using ferric oxide hydrosols prepared by a method given by Thomas and Frieden.[68] This method consisted of adding, drop by drop, 14-molar ammonium hydroxide solution from a burette to a 3-molar solution of ferric chloride that was kept continuously agitated. The ammonium hydroxide was added until the precipitate peptized with great difficulty. Complete precipitation of the ferric oxide hydrosols in this case, also, took place upon adding the various salts up to the concentration of the salts in sea water.

These experiments show that ferric oxide sols of concentrations such as might exist in natural waters are precipitated almost immediately by the electrolytes of the sea.

A further experiment was carried out on the precipitation of ferric oxide by electrolytes of the sea. A 50-c.c. sample of ferrous bicarbonate solution formed by carbonated water acting on 10-mesh norite for 287 days was obtained. The solution contained 27.2 parts per million iron, calculated as ferric hydroxide. One c.c. of peat solution containing 922 parts per million organic matter was added to the sample. Thus the total reaction mixture of 51 c.c. contained about 27 parts per million iron, calculated as ferric oxide, and 16 parts per million organic matter. Air was bubbled through the solution for three days, causing the iron in solution as bicarbonate to lose its carbon

[68] Thomas, A. W., and Frieden, A., *Jour. Amer. Chem. Soc.*, 45, p. 2523, 1923.

dioxide. The finely divided ferric oxide, however, instead of precipitating remained as ferric oxide hydrosol stabilized by the organic colloids of the peat solution. Sea salt in the proportion of 34,400 parts per million was added to this natural-formed ferric oxide hydrosol. There was no noticeable change in the solution at the time of adding the sea salt but after a few hours it became very cloudy, and at the end of three days a flocculent, reddish brown, gelatinous mass of ferric hydroxide had settled to the bottom of the tube.

This experiment is of exceptional importance geologically for it shows the precipitating effect of ocean electrolytes on a ferric oxide hydrosol that had been formed by natural means only.

Precipitation of Iron from Organic Iron Solutions by Bacteria.—It has long been known that certain bacteria have the power of taking iron from solution and precipitating it as ferric hydroxide. Since the time of Ehienberg, 1836, much has been written regarding the morphology and physiologic processes of bacteria but only within recent years has the importance of these organisms in the formation of iron ore deposits been recognized.

Students of geology owe a great deal to Harder[69] for his excellent treatise, and especially for the very complete bibliography that he has assembled.

Harder has divided the iron-depositing bacteria into three main groups:

1. "Iron bacteria that precipitate ferric hydroxide from solutions of ferrous bicarbonate, using the carbon dioxide set free and the available energy of the reaction for their life processes." *Spirophyllum ferrugineum* belongs to this group and probably *Gallionella ferruginea*. *Spirophyllum ferrugineum* does not grow in media that do not contain ferrous bicarbonate. The less organic matter present the better this bacterium thrives, and abundant carbon dioxide increases growth.

2. "Iron bacteria that do not require ferrous bicarbonate for their life processes, but cause the deposition of ferric hydroxide when either inorganic or organic iron salts are present."

[69] Harder, E. C., The Iron Depositing Bacteria and their Geologic Relations, U. S. Geol. Surv. Prof. Paper 113, 1919.

The most important of this group are *Leptothrix ochracea* and *Cladothrix dichotoma. Leptothrix ochracea,* (as *Spirophyllum ferrugineum*) is an anerobic organism occurring abundantly in iron-bearing waters of iron springs and marshes, and controlled to a large extent by the presence of iron salts and organic matter. The organic matter appears to be required as a source of carbon. *Cladothrix dichotoma* is a widespread soil organism which has the power of depositing iron on its sheath.

3. "Iron bacteria that attack organic iron salts, using the organic acid radicle as food and precipitating ferric hydroxide, or basic ferric salts, which are gradually changed to ferric hydroxide." This group probably consists of lower bacterial forms. Some attack only one or two organic salts, while others are able to use a large number, including humates.

Harder [70] was able to isolate several of these forms, which were able to precipitate ferric hydroxide from solutions of ferric ammonium citrate but only these. He did show, however, that practically all soils and natural waters contain bacteria that are capable of precipitating ferric hydroxide or basic salts from solutions of ferric ammonium citrate, ferric citrate, ferric oxalate, and iron lactate. He experimented, also, with inorganic iron salts, as ferrous sulphate, ferrous ammonium sulphate, ferrous carbonate, and ferric chloride. Precipitation occurred in all these inorganic solutions but it seemed to be due to oxidation and hydrolysis or to hydrolysis alone rather than to biologic processes.

A series of experiments was carried out to determine whether soil bacteria would precipitate ferric hydroxide from organic iron solutions other than those used by Harder.[71] The experiments showed that bacteria in soil and muck obtained from widely separated localities precipitate ferric hydroxide from ferric ammonium tartrate, ferric tartrate, ferric formate, and ferric malate.

The method used in determining whether or not the precipitation is due to biological agencies was that devised by Harder.[72]

Three flasks and two glass jars, were filled as follows: In the

[70] *Idem,* p. 36.
[71] *Idem,* p. 39.
[72] *Idem,* pp. 31–33.

bottom of jar No. 1 was placed ten grams of muck that was collected from the marsh along the Holland river, Holland Landing, Ontario. In the bottom of jar No. 4 was placed ten grams of soil that was obtained from the banks of the Don river, Riverdale Park, Toronto. The material in both these jars was covered by a filter paper. Flask No. 5 was filled with hay extract—that is, water in which hay had been boiled. Flask No. 2 was filled with water from the city supply of Toronto and flask No. 3 with distilled water. To each of the jars and flasks was added one gram of ferric ammonium tartrate. The jars and flasks each contained 250 c.c. of solution. They were allowed to stand at room temperature for two weeks and were then examined. The solution in jar No. 1 had become decidedly lighter in color, and a layer of flocculent material, yellowish red in color, had been deposited. The result in jar No. 4 was similar to that in jar No. 1. The solution in flask No. 2 had become slightly darker, showing that some bacterial action had taken place. The solution in flask No. 5, containing the hay extract, had turned a dirty brown and showed a distinct brown precipitate on the bottom. There was no evidence of change in flask No. 3, containing distilled water.

The jars and flasks were again examined at the end of a month. The solution in jar No. 1 had become perfectly clear and transparent. A thick deposit of ferric hydroxide with perhaps some basic ferric salt had appeared on the filter, and tufts of ferric hydroxide were attached to the inside surface of the jar. Similar results were shown in jar No. 4. All the iron had been precipitated in flask No. 5, but the solution still remained a dirty, dark color, due to the hay extract. The solution in flask No. 2 had become quite dark, although no precipitation had taken place, showing that some bacterial action had been set up. No recognizable change was seen in flask No. 3.

The jars and flasks were photographed at the end of three months. The only noticeable changes after standing this additional time were that flask No. 2, containing water from the Toronto supply, had become quite dark and a slight precipitate

had appeared on the bottom of the flask, and flask No. 3, which contained distilled water, had become considerably darker than a freshly prepared solution.

The above results indicate that the iron had been precipitated from the ferric ammonium tartrate, either by some unknown action of the muck and soil on the respective solutions, or else due to some biologic agency.

Precipitation of some organic and inorganic iron salts may take place by oxidation and hydrolysis, or by hydrolysis alone; the precipitate consisting either of their hydroxides or of basic ferric salts. It is fairly safe to conclude, however, that precipitation did not occur in this manner in the experiments cited above, for there was no evidence of precipitation of the iron from the distilled water solution.

In order to be as certain as possible that the precipitation of the ferric ammonium tartrate solutions was due to bacterial agencies alone, fresh solutions of the salt were innoculated with the muck and soil and placed in an autoclave at 130° Centigrade for fifteen minutes. The sterilized solutions were then set away at room temperature and examined at frequent intervals for signs of precipitation. There was no evidence of precipitation at the end of three months.

The sterilized solutions were again innoculated with fresh muck and soil in order to see whether the ferric ammonium tartrate would still be susceptible to bacterial action. Complete precipitation occurred at the end of a month.

These experiments prove conclusively that muck from the Holland river and soil from the Don river, contain bacteria that are able to precipitate ferric ammonium tartrate solutions.

The precipitates consisted of a textureless colloidal mass of ferric hydroxide, that at first resembled the ferric hydroxide precipitated by ammonia, but gradually changed to a more dense yellow material resembling closely the bog iron ore from Calumet lake, Quebec. The precipitate may have contained some basic ferric tartrate, but it did not give any test for this salt. It is quite probable that had the precipitate been examined im-

mediately upon its formation some basic salt would have been detected, but upon standing this basic salt was subject to further bacterial action, and it altered to hydroxide. The precipitate under close microscopic examination showed absolutely no evidence of bacteria, which is probably due to the small size of the organisms, or to the possibility that they were still in the supernatant liquid.

The experiments performed with ferric ammonium tartrate were conducted also with ferric malate, ferric formate, and ferric tartrate. Similar results were obtained. The ferric malate required considerable time to go into solution, so the salt was placed in the required quantity of distilled water and shaken at intervals until solution was complete, when it was inoculated with the muck and soil.

The jars were examined at frequentt intervals during the three months incubation. Partial precipitation occurred at the end of two weeks in jars Nos. B 1, and B 4, but complete precipitation did not occur until the end of five weeks. In each case the precipitate on the filter consisted of a thin layer of reddish brown oxide of iron, with tufts of iron oxide on the sides of the jars. A light brown, brittle film developed on the surface of the solution in jar B 4 and from it brown filaments extended down into the solution. These films probably consisted of moulds. The precipitate, on microscopic examination, consisted of a textureless mass that showed no evidence of bacteria but did show some evidence of moulds. The solution in flask No. B 2, became, at the end of two weeks, slightly darker in color, and peculiar spherical, white, fluffy masses had commenced to develop in the solution. These fluffy masses in three months became quite numerous, but the solution did not change in color to any appreciable extent. Under the microscope these masses consisted of a lattice-like growth, and they were probably moulds. There was no indication of iron in the sheath. The solution in flask B 3 underwent almost the same change except that it did not become quite so dark. There was no evidence, even at the end of three months, of any of the iron having been precipitated. The solution in jar

No. B 6, which was sterilized after the muck was added, showed no evidence of precipitation during its period of incubation, but upon addition of a fresh supply of muck, precipitation occurred as before, in about four weeks.

Precipitation was noticeable in jars Nos. C 1, and C 4, at the end of one week, but it did not become complete until the end of twelve days, when the solutions became perfectly clear. There were no indications of films of any kind on the surfaces of the liquids. The precipitates were reddish brown and very flocculent and only a very small percentage adhered to the sides of the vessels. Under the microscope these precipitates were a yellow color and consisted of colloidal ferric hydroxide. There was no indication of organisms of any kind in the precipitates. The only noticeable changes in C 2 and C 3 were in the colors of the solutions, which were altered from reddish brown to brownish orange, and were considerably less clear, expecially C 2, which contained tap water. There was no evidence of precipitation in C 2, or C 3, although some bacterial action must have taken place to so change the color. The sterilized solution in jar No. C 6, which also contained muck, precipitated. The precipitation, in this case, however, was not due to bacterial action but to the fact that the solution was unable to stand the temperature necessary for sterilization. When taken from the autoclave precipitation had already occurred. The precipitate, which was due to the hydrolysis of the ferric formate, was flocculent and of a dirty green color.

The failure of C 6 to withstand the temperature of sterilization makes it difficult to prove definitely that ferric formate solutions are precipitated by bacterial agencies. Bacterial agencies were in all probability the cause of the precipitation, because the solutions in distilled water and tap water remained practically unaltered after standing three months, whereas those inoculated with muck and soil precipitated within one and one-half weeks. It might be possible to repeat the sterilizing experiment with better success by sterilizing at lower temperature and for a longer time.

Some precipitation occurred at the end of one week in D 1 and D 4, but it was not until after three weeks that it was complete. The solutions became clear although they appeared otherwise, as considerable of the precipitate separated out on the sides of the vessels. There was a thin, yellowish brown scum on the surfaces of the liquids. The precipitate formed a thin, yellowish brown layer that very closely resembled bog iron ore. This precipitate consisted chiefly of hydrated ferric oxide, as no test for basic ferric tartrate could be obtained.

A partial analysis of the precipitate gave the following results:

(Dried at 105°C.)	
Ferric Oxide (Fe_2O_3)	83.62
Combined water	17.85
	101.47

It appears, therefore, from this partial analysis that the material is one of the more hydrated forms of ferric oxide. A percentage of 14.5 combined water requires 85.5 per cent. of ferric oxide to form limonite ($2Fe_2O_3, 3H_2O$).

Precipitation occurred in D 2 and D 3, although D 2 was a solution of ferric tartrate in tap water and D 3, a solution in distilled water. This precipitation, however, was only slightly noticeable after one month's incubation and was not complete until after two months. In contrast with these results the solutions in D 1 and D 4, containing muck and soil, were completely precipitated in three weeks. The precipitation, therefore, of the solution in D 2 and D 3 is not due to biologic agencies. The character of the precipitate is also very different. As stated previously, the precipitate in D 1 and D 4 consists of a thin, compact, yellowish brown layer, whereas that in D 2 and D 3 consists of a thick, gelatinous mass resembling the ferric hydroxide precipitated by ammonia. There is little doubt that this precipitation is due to straight hydrolysis of the ferric tartrate; the precipitation by hydrolysis requiring considerably more time than the precipitation by bacterial action.

The solution in D 6 was allowed to incubate for only one

month. This solution was sterilized, and it shows very clearly that, up to this time, precipitation by bacteria did not occur and that precipitation by hydrolysis did not take place to any appreciable extent. When D 6 was reinoculated with muck, precipitation occurred as before, in about three weeks.

The experiments performed show very conclusively that iron is precipitated as ferric hydroxide, with perhaps some basic ferric salts, from solutions of ferric ammonium tartrate, ferric malate, ferric formate, and ferric tartrate, by the organisms in the Holland Landing muck and the Don river soil. The muck and soil were obtained from widely different localities and, therefore, soil organisms that precipitate ferric hydroxide from organic iron solutions are extremely common. The time of precipitation of each salt varies considerably, the range being one and one-half weeks for ferric formate, five weeks for ferric malate and three to four weeks respectively for ferric tartrate, and ferric ammonium tartrate.

It was thought that light might have some effect on the rate of precipitation of the various iron salts, so samples of the ferric ammonium tartrate, ferric formate, ferric malate, and tartrate were inoculated with soil and set in a dark box. The solutions precipitated as before, and in approximately the same length of time.

Harder's [73] experiment of passing carbon dioxide through a solution of ferric ammonium citrate, inoculated with soil, was repeated with ferric ammonium tartrate, ferric malate, ferric formate and ferric tartrate solutions, and complete precipitation of the solutions occurred as it did in his experiments.

The above experiments were reconducted, but instead of passing carbon dioxide through the solutions, oxygen was passed through them. Precipitation occurred also in this case, the time required being approximately the same as for the original experiments.

Harder [74] performed several experiments with the object of determining whether organisms in pure natural waters can pre-

[73] Harder, E. C., U. S. Geological Survey Prof. Paper 113, p. 33.

[74] *Idem*, p. 31.

cipitate iron from ferric ammonium citrate solutions. He found that organisms in water from Lake Mindota were able to precipitate the iron within a month. The organisms in these waters, however, were unable to precipitate the iron from solutions of ferric citrate, ferric oxalate, iron lactate and iron acetate.[75] A series of experiments was carried out to determine whether organisms in natural waters from Calumet lake, Quebec, and Hematite lake, Ontario, can precipitate ferric ammonium tartrate solutions. To 500 c.c. of the respective waters was added two grams of ferric ammonium tartrate. The solutions were examined at the end of two weeks, but there was no evidence of precipitation. A portion of the iron precipitated as hydroxide at the end of one month, but it was not until after four months that all the iron came down. Duplicate samples in distilled water remained unchanged except that they became darker in color. Sterilized samples of the waters containing ferric ammonium tartrate remained unchanged. These experiments were conducted also with ferric formate, ferric malate, and ferric tartrate solutions, but up to the time of observation, six months, complete precipitation occurred only in the case of the ferric tartrate solution. This precipitation occurred at the end of two months and it was probably due to hydrolysis, as was the case with ferric tartrate in distilled water solution.

These experiments show that ferric ammonium tartrate is precipitated as ferric hydroxide by bacteria in natural waters such as those of Hematite and Calumet lakes.

PRECIPATION OF COLLOIDAL SILICA.

Precipitation in Sodium Silicate Solutions.

Precipitation by Electrolytes.—Recently considerable experimental work has been done on the precipitation of silica by electrolytes from dilute sodium silicate solutions. In practically every case different results have been obtained.

Tarr [76] states that the colloidal silica carried to the sea by rivers

[75] *Idem*, p. 38.

[76] Tarr, W. A., *Amer. Jour. Sci.*, 44, p. 431–436, 1917. University of Missouri Studies, vol. 1, No. 1, p. 24, 1926.

and not precipitated with the clays is coagulated by the positive charged ions of sodium, potassium, calcium, and magnesium neutralizing the negative charges on the colloidal silica particles. He substantiated this statement by several experiments, as follows:

1. A solution of NaCl, $MgSO_4$ and K_2SO_4 in the proportions in which they occur in sea water was made with a total salinity of 34,400 parts per million. Silica, in the form of water glass, was added to this solution in the proportion of 27.07 parts per million. A heavy precipitate of gelatinous silica was immediately obtained.

2. To brine of sodium chloride containing 34,400 parts per million, silica in the form of water glass was added in the proportion of 27.07 parts per million. A precipitate of silica gel formed immediately but it was less heavy than in Experiment 1.

3. This experiment was similar to Experiment 1 except that just one-half the amount of water glass was used. In this case also a heavy precipitate was immediately obtained.

4. This experiment was similar to Experiment 2 except that twice the quantity of water glass was used. A precipitate, but not heavy, was formed immediately.

5. Magnesium sulphate in the proportion found in sea water was added to half the solution used in Experiment 4. The result was an immediate and large increase in the coagulated material.

Lovering,[77] from a series of experiments reached conclusions opposite to those of Tarr. He found that acids, carbonated water or alkalies dissolved silica in cold solutions; the acids acting most effectively on silicates, alkalies on opal and chalcedony, and solutions of magnesium or calcium bicarbonates on quartz, jasper and taconite. He tried to repeat Tarr's experiments but did not obtain similar results. In contrast to Tarr's artificial solutions, however, he used natural sea water. His experiments were as follows:

1. A solution containing 35 parts per million silica in the form of sodium silicate was made and to it was added 10 c.c. of sea

[77] Lovering, T. S., Econ. Geol., 18, p. 537. 1923.

water. The solution was filtered and the residue and filtrate analyzed for silica. There was no silica in the residue and 36 parts per million was still in the filtrate. This experiment was reconducted using 50 c.c. of sea water and practically the same results were obtained.

2. A solution containing 490 parts per million silica in the form of sodium silicate was made, and to it was added 10 c.c. of sea water. A precipitate occurred immediately. On analysis the precipitate contained 0.014 grams of silica and the filtrate 0.0144 grams, showing that 288 parts per million silica still remained in solution. Another experiment was performed using 50 c.c. of sea water, and similar results were obtained.

3. 50 c.c. of moderately strong sodium silicate solution, containing between 6,000 and 8,000 parts per million silica, was made. To this solution was added 10 c.c. of sea water. A precipitate immediately formed. The solution was filtered and the residue and filtrate analyzed for silica. The residue contained 0.1534 grams of silica and the filtrate 0.0404 grams, showing that 3108 parts per million silica was thrown down while 808 parts per million still remained in solution, on recalculation to the 50 c.c. basis. This experiment was repeated with a slightly more dilute sodium silicate solution and 50 c.c. of sea water added. Precipitation, in this case, was caused by 9 c.c. of sea water, the other 41 c.c. serving only to dilute the solution.

Lovering concluded that one c.c. of sea water is capable of precipitating 0.0155 grams of silica from a sodium silicate solution providing the concentration of the solution is high enough. Complete precipitation never occurs, and in dilute solutions containing up to 36 parts per million silica no precipitation occurs. He further concluded that 275 parts per million silica may remain dissolved in a slightly alkaline solution in the presence of rather large quantities of electrolytes.

In order to determine, if possible, the reasons for the difference in the above results of Tarr and Lovering a series of experiments was conducted.

Commercial water glass, which is a concentrated solution of

sodium silicate, was diluted to a specific gravity of 1.0684, and 50 c.c. of this solution was analyzed, giving 1.2868 grams of silica. The prepared solution consequently contained 25,736 parts per million silica. A portion of this water glass solution was diluted 857 times giving a solution containing 30 parts per million silica. Whether the silica is in the form of sodium silicate or colloidal silica is yet to be determined. The following electrolytes in the proportion of the electrolytes in sea water, that is, 34,400 parts per million were added to 200-c.c. samples of the above solution. Each sample contained 30 parts per million silica. The following results were obtained:

1. A solution containing only 30 parts per million of silica. No result.

2. Sodium chloride (34,400 parts per million). No indication of a precipitate.

3. Potassium sulphate (34,400 parts per million). No indication of a precipitate.

4. Magnesium sulphate (34,400 parts per million). No indication of a precipitate.

5. Carbon dioxide passed through the solution for one hour. A precipitate formed which disappeared in a few hours.

6. Calcium carbonate was added and then carbon dioxide passed through the solution for one hour. No indication of a precipitate.

7. Salt, obtained from the evaporation of natural sea water, added in the proportion of 34,400 parts per million. A very slight indication of a precipitate.

The results of these experiments seemed to be rather more in accord with those of Lovering than with those of Tarr. To make certain of the results they were repeated and similar results were obtained. The experiments show that sodium silicate solutions, containing 30 parts per million silica are not precipitated immediately by electrolytes such as are in sea water. In order to determine if time has any influence on the precipitating effect of the electrolytes, the two sets of solutions were set away and examined at the end of 25 and 75 days, respectively. A slight

precipitate appeared in several of the test tubes. Since 30 parts per million is a very dilute solution it was thought best to filter the solutions and analyze both the filtrate and precipitate for silica. The results obtained are given in Table II. Each silica determination was made by evaporating twice with hydrochloric acid and then hydrofluorizing the silica.

TABLE II.

EXPERIMENTS ON SODIUM SILICATE SOLUTIONS WHICH CONTAIN 30 PARTS PER MILLION SILICA.

Exp.	Salt, etc., in Solution with Sodium Silicate	Time in Days	Gms. SiO_2 in Precipitate	Gms. SiO_2 in Filtrate	SiO_2 in Precipitate, Recalculated to Parts per Million	Parts per Million SiO_2 in Filtrate
1 *A*	Blank	25	0.0003	0.0059	1.5	29.5
B	"	75	0.0007	0.0054	3.5	27.0
2 *A*	NaCl, 34,400	25	0.0010	0.0056	5.0	28.0
B	p.p.m.	75	0.0015	0.0050	7.5	25.0
3 *A*	K_2SO_4, 34,400	25	0.0008	0.0057	4.0	28.5
B	p.p.m.	75	0.0016	0.0049	8.0	24.5
4 *A*	$MgSO_4$, 34,400	25	0.0009	0.0057	4.5	28.5
B	p.p.m.	75	0.0008	0.0056	4.0	28.0
5 *A*	CO_2 Passed through	25	0.0002	0.0062	1.0	31.0
B	1 hr.	75	0.0003	0.0063	1.5	31.5
6 *A*	$CaCO_3+CO_2$ for 1	25	0.0013	0.0051	6.5	25.5
B	hr.	75	0.0024	0.0039	12.0	19.5
7 *A*	Sea salt, 34,400	25	0.0018	0.0043	9.0	21.5
B	p.p.m.	75	0.0032	0.0034	16.0	17.0

From a study of Table II it is seen that in all cases part of the silica has been thrown down, with the possible exceptions of 5 A and B. In these two cases it appears as if the carbon dioxide acts as a peptizing agent, since with 1 A and B, containing only sodium silicate, an appreciable precipitation occurred. Sea salt and calcium bicarbonate have the greatest precipitating effect. Contrary to expectation, magnesium sulphate has little effect on the solutions. The experiments show conclusively that time plays a very important part in the precipitation of silica by electrolytes from dilute sodium silicate solutions and that although

at the end of 75 days considerable silica has been thrown down, a high percentage still remains in solution.

A solution containing 30 parts per million silica is very dilute, and consequently if precipitation occurs it is difficult to observe. For this reason the above experiments were reconducted using solutions of sodium silicate containing a higher percentage of silica. Part of the prepared sodium silicate solution was diluted in such a ratio that it contained 500 parts per million silica. Samples containing 50 c.c. were placed in test tubes and the chosen electrolyte added. The results follow:

1. Solution containing silica only in proportion of 500 parts per million.

2. Sodium chloride (34,400 parts per million). Slight precipitate.

3. Potassium sulphate, same proportion. No indication of a precipitate.

4. Magnesium sulphate, same proportion. A white, heavy precipitate immediately came down.

5. Carbon dioxide passed through the solution for one hour. A white precipitate resulted, but disappeared upon standing for a few hours.

6. Calcium carbonate added, and carbon dioxide passed through the solution for one hour. No indication of a precipitate.

7. Sea salt (34,400 parts per million). No indication of a precipitate.

These experiments show that of all the electrolytes used, magnesium sulphate is the only one that produced a permanent precipitate. This precipitate was a white, textureless mass, and it did not have the appearance of true gelatinous colloidal silica. Possibly this is the type of precipitate that Tarr obtained in his experiments, for it is significant that whenever he used magnesium sulphate a voluminous precipitate formed. This result leads one to suppose that Tarr used a higher concentration of sodium silicate than he was aware of in his experiments.

The solutions were set aside for 75 days and the results are given below:

No. 1, containing only sodium silicate, showed only a very slight indication of a precipitate.

No. 2, containing sodium chloride, showed an appreciable precipitate of colloidal silica.

No. 3, containing potassium sulphate, showed a slight indication of a precipitate.

No. 4, containing magnesium sulphate, showed the white, compact precipitate that formed immediately on addition of magnesium sulphate.

No. 5, carbon dioxide bubbled through the solution for an hour, showed no indication of a precipitate.

No. 6, calcium carbonate added and carbon dioxide passed through the solution for one hour. A thick gelatinous layer of colloidal silica was deposited. The compact layer of calcium carbonate was seen below this layer of gelatinous silica.

No. 7, containing sea water, showed also a thick layer of gelatinous silica.

These solutions were examined periodically, and it was found that the colloidal silica did not separate at once, but accumulated gradually.

The results show clearly the comparison between the gelatinous silica thrown down with time by electrolytes from sodium silicate solutions, and the compact precipitate that formed immediately upon the addition of magnesium sulphate.

The results of these experiments confirm the results of the first set of experiments in which sodium silicate solutions containing 30 parts per million silica were used, in that calcium bicarbonate and sea water are two of the best precipitants of colloidal silica from sodium silicate solutions. Sodium chloride and potassium sulphate are not such powerful precipitants. Time is one of the important factors in the precipitation of colloidal silica.

The solutions were not analyzed for silica.

Precipitation by Magnesium Sulphate.—One of the outstanding features in the experiments to date is the action of magnesium sulphate on sodium silicate solutions of various concentrations. Magnesium sulphate, when added to a solution of sodium silicate

containing 30 parts per million silica, gives practically no precipitate even if the solution is allowed to stand for 75 days. A heavy, white precipitate forms immediately, however, when magnesium sulphate is added to a sodium silicate solution containing 500 parts per million.

It was thought that this precipitate might be magnesium silicate and that our ideas regarding the dilutions at which sodium silicate is completely hydrolyzed would have to be altered.

Thorpe [78] states that aqueous solutions of aluminium chloride and sodium silicate react to form a precipitate of the composition $2Al_2O_3.3SiO_2$, which adsorbs silica and in the presence of sufficient silicic acid is converted into the compound $Al_2O_3.2SiO_2$, analogous to kaolin. Muir and Morley [79] found that $MgSiO_3.XH_2O$ is obtained by precipitating aqueous sodium silicate by dilute magnesium chloride. Van Hise and Leith [80] point out also that ferrous sulphate reacts directly with solutions of the silicates of the alkalies, giving a granular precipitate of the composition $FeO.2SiO_2$. These results show that it is possible to obtain silicates in reactions between different salts and sodium silicate solutions provided the solutions are of such a concentration that complete hydrolysis has not taken place, for in sodium silicate solutions that are hydrolyzed by dilute HCl no precipitate forms.

Kohlrausch [81] was the first to advance the idea that in dilute solutions sodium silicate is at least partly hydrolyzed. He reached his conclusions from studying the electrical conductivity of solutions of sodium silicate having the formulae Na_2SiO_3 and $Na_2O.3.4SiO_2$. His conclusions, although partially correct, were founded on erroneous experimental evidence, since more recently McBain and Salman [82] have shown that " Colloidal electrolytes are salts in which an ion has been replaced by a heavily hydrated polyvalent micelle that carries an equivalent sum-total of electrical

[78] Thorpe, E., Dictionary of Applied Chemistry, vol. VI., p. 249.

[79] Muir, M. M. P., and Morley, H. F., Watt's Dictionary of Chemistry, No. 4, p. 453, 1894.

[80] Van Hise, C. R., and Leith, C. K., U. S. Geol. Surv. Mon. 52, p. 521.

[81] Kohlrausch, F., *Zeit. Phys. Chem.*, 12, p. 773, 1894.

[82] McBain, J. W., and Salman, C. S., *Jour. Chem. Soc.*, 42, p. 427, 1920.

charges and conducts electricity just as well or even better than the simple ion it replaces." Kahlenberg and Lincoln examined solutions of sodium silicate and by data obtained by freezing point determinations concluded that solutions of sodium silicates are hydrolytically decomposed into sodium hydroxide and colloidal silicic acid. Complete hydrolysis takes place when one gram-molecule is contained in 48 litres, that is, at a dilution of 2549 parts per million sodium silicate, which is equivalent to 1257 parts per million silica.

This result of Kahlenberg and Lincoln,[83] giving complete hydrolysis of sodium silicate solutions at a dilution of 1257 parts per million silica, appears to be too high. Sodium silicate solutions containing 480 parts per million silica react with aqueous magnesium sulphate solutions, forming immediately a dense white precipitate. This white precipitate may be magnesium silicate formed by the interaction between magnesium sulphate and sodium silicate in true solution. If such an interaction can be proved then sodium silicate solutions at dilutions as low as 480 parts per million silica are only partially hydrolyzed to colloidal silica and sodium hydroxide. Evidence in favor of this assumption is that if a sodium silicate solution is first hydrolyzed by hydrochloric acid and then magnesium sulphate added, no precipitate forms even when the solution is boiled. A series of experiments was performed to determine whether the precipitate mentioned above was magnesium silicate and also, if possible, to determine the dilution at which complete hydrolysis of sodium silicate takes place.

A solution of sodium silicate containing 480 parts per million silica was made by diluting a strong solution of known concentration. A 100-c.c. portion of this solution was divided into two 50-c.c. portions and to one of these fractions, containing 480 parts per million silica, magnesium sulphate in the proportion of 34,400 parts per million was added. The remaining 50-c.c. portion was divided into two parts, one part being made up to 50 c.c., thus having a concentration of 240 parts per million silica. This

[83] Kahlenberg, L., and Lincoln, A. T., *Jour. Phys. Chem.*, 2, p. 77, 1898.

process of subdivision was continued until 50-c.c. samples containing 120, 60, and 30, parts per million silica were obtained. A solution containing 85 parts per million also was made. Magnesium sulphate in the proportion of 34,400 parts per million was added to each sample. The results obtained on the addition of the magnesium sulphate are indicated below:

1. Sodium silicate solution containing 480 parts per million silica. A white gra...lar precipitate formed at once.

2. Sodium silicate solution containing 240 parts per million silica. A white granular precipitate appeared, but it was not nearly so heavy as in No. 1.

3. Sodium silicate solution containing 120 parts per million silica. No indication of a precipitate at first but inside of 15 minutes a very appreciable precipitate formed.

4. Sodium silicate solution containing 85 parts per million silica. No indication of a precipitate upon the addition of magnesium sulphate, but inside of three hours a precipitate was very noticeable.

5. Sodium silicate solution containing 60 parts per million silica. There was no indication of a precipitate until the next day, and it was not very heavy.

6. Sodium silicate solution containing 30 parts per million silica. At the end of 3 days there was practically no indication of a precipitate.

These experiments show that magnesium sulphate does not produce a precipitate from solution of sodium silicate containing less than 30 parts per million silica, but that with increasing concentration a heavy, white, granular precipitate is formed.

In order to determine the constitution of the precipitate produced and also to determine the amount of silica still in solution, the set of solutions was filtered and the precipitates and filtrates analyzed. The results of the silica analyses are given in Table III.

TABLE III.

PRECIPITATION OF SODIUM SILICATE SOLUTIONS BY MAGNESIUM SULPHATE WHICH HAD BEEN ADDED IN THE PROPORTION OF 34,400 PARTS PER MILLION.

Exp.	P.p.m. SiO_2 in Solution.	Time in Days.	Gms. SiO_2 in Precipitate.	SiO_2 in Precipitate Calculated to Original p.p.m.	Gms. SiO_2 in Filtrate.	P.p.m. SiO_2 in Filtrate.
1	480	3	0.0141	282	0.0052	104
2	240	3	0.0070	140	0.0054	108
3	120	3	0.0015	30	0.0048	96
4	85	3	0.0010	20	0.0034	68
5	60	3	0.0006	12	0.0024	48
6	30	3	0.0003	6	0.0014	28

On examination of the above table it is seen that the silica has not all been precipitated; amounts ranging from 104 to 28 parts per million still remain in solution. These quantities probably represent the proportion of the sodium silicate that is hydrolyzed. The constant values obtained in Experiments 1, 2, and 3 seem to indicate that solutions of sodium silicate having concentrations of at least 120 parts per million silica undergo the same amount of hydrolysis. The values obtained in Experiments 4, 5, and 6 indicate that with concentrations below 120 parts per million silica the amount of hydrolysis gradually increases until with solutions below 30 parts per million it is complete. This value for the dilution at which sodium silicate is completely hydrolyzed agrees with that obtained by Bogue.[84] He found, in studying the hydrogen ion concentrations of the silicates of sodium, that at a dilution of one gram molecule in 100 litres a relatively small value was obtained for the percentage of hydrolytic dissociation. This value was very low in comparison with those results obtained by Kohlrausch, and Kahlenberg and Lincoln, by the conductivity and freezing point methods. Bogue obtained hydrolytic dissociations ranging from 1.58 to 28.43 per cent. at a dilution of 1223 parts per million sodium silicate, which vary respectively in their $Na_2O : SiO_2$-ratio from 1 : 4 to 1 : 1. Twelve hundred and twenty-three parts per million sodium silicate is equivalent to 603

[84] Bogue, R. H., *Jour. Amer. Chem. Soc.*, 42, p. 2575, 1920.

parts per million silica. A recalculation of Bogue's results, averaging the percentage hydrolyzing, shows that only 90 parts per million of the silica is hydrolyzed when a sodium silicate solution contains 603 parts per million silica. This value is very close to those obtained in Table III, Experiments 1, 2, and 3, in which 104, 108, and 96 parts per million silica remained in solution due to the hydrolysis of sodium silicate solutions containing 480, 240, and 120 parts per million silica, respectively.

Geologists have generally accepted the conclusions of Kahlenberg and Lincoln that complete hydrolysis of the silicates of the alkalies takes place at a dilution of 2,549 parts per million. Consequently at dilutions such as exist in nature—rivers very seldom carry more than 35 parts per million silica—complete hydrolysis has taken place in practically every case, and the silica is almost all in the colloidal form. The results obtained by Bogue and those given above indicate that our ideas as to the dilution at which complete hydrolysis of the alkaline silicates takes place can be altered and that there is a possibility that part of the silica carried by rivers containing a high percentage of silica is carried as alkaline silicate, although the percentage is very small compared to that carried as colloidal silica. It appears, therefore, that there is some ground for Dienert's [85] statement that silica is carried in solution as alkaline silicate and that on separation of the alkali the silica is thrown down.

There is little doubt that magnesium silicate is precipitated when magnesium sulphate solutions are added to sodium silicate solutions. The precipitates from Experiments 1, 2, and 3, Table III, were analyzed in order to be certain of this point. The results are given below.

	1.	2.	3.
MgO	25.00	14.3	14.25
SiO_2	75.35	84.2	83.16
CaO	trace	trace	trace
Fe_2O_3	trace	trace	trace
Sulphate	trace	trace	trace

[85] Dienert, M. F., *Bull. Soc. Chem.*, 4th ser. 13, pp. 381–394, 1913.

Analysis 1 gives a compound of the formula $MgO.2SiO_2$, while 2 and 3 give compounds of the formula $MgO.4SiO_2$. It is quite probable that the true compound is $MgO.SiO_2$ with excess silica. Column No. 1 represents the mean of three analyses, so there can be little doubt that magnesium silicate and not colloidal silica is precipitated when magnesium sulphate is added to a solution of sodium silicate containing 480 parts per million silica.

PRECIPITATION OF SILICA HYDROSOLS.

Formed by Dialyzing a Solution of Sodium Silicate.

In the previous section it has been shown that sodium silicate hydrolyses to colloidal silica and sodium hydroxide, and that the percentage hydrolysing increases with the dilution of the solution. These results led the writers to prepare a colloidal silica solution by the direct dialysis of sodium silicate, and to test the precipitating effect on it of different electrolytes. A solution of water glass containing 25,736 parts per million silica was dialyzed until free from electrolytes. The dialyzed colloidal solution was then analyzed and found to contain 1,480 parts per million silica showing that at least 16/17 of the silica had escaped as ionic silica.

Precipitation by electrolytes.—A portion of the colloidal silica solution was diluted in such a manner that a solution containing 30 parts per million silica was obtained. The chosen electrolytes were added to 200-c.c. samples with the following results:

A 1, Blank, containing only the colloidal silica.

B 1, NaCl (34,400 parts per million). No evidence of a precipitate at the time salt was added.

C 1, Magnesium sulphate (34,400 parts per million). No evidence of a precipitate.

D 1, Sea salt (34,400 parts per million). No evidence of a precipitate.

E 1, Magnesium carbonate and carbon dioxide for one hour. No evidence of a precipitate.

F 1, Calcium carbonate and carbon dioxide for one hour. No evidence of a precipitate.

The above set of experiments was repeated and the two sets

of solutions were set away and periodically examined. Precipitates were noticed at the end of 75 days by sight only in B 1 and D 1, but they were only very slight. This was to be expected at such a low dilution as 30 parts per million. The first set was filtered at the end of 25 days and the filtrates and precipitates analyzed for silica. The second set was filtered and analyzed at the end of 75 days.

The contents of the precipitates and filtrates analyzed are given in the following table: Table IV.

TABLE IV.

EXPERIMENTS ON DIALYZED SODIUM SILICATE SOLUTIONS CONTAINING 30 PARTS PER MILLION SILICA.

Exp.	Salt, etc., in Solution with Colloidal SiO_2.	Time in Days.	Gms. SiO_2 in Precipitate.	Gms. SiO_2 in Filtrate.	SiO_2 in Precipitate, Recalculated to p.p.m.	P.p.m. SiO_2 in Filtrate.
A 1	Blank	25	0.0002	0.0055	1.0	27.5
2	"	75	0.0005	0.0051	2.5	25.5
B 1	NaCl, 34,400 p.p.m.	25	0.0020	0.0047	10.0	23.5
2		75	0.0041	0.0023	20.5	11.5
C 1	$MgSO_4$, 34,400	25	0.0003	0.0056	1.5	28.0
2	p.p.m.	75	0.0002	0.0057	1.0	28.5
D 1	Sea salt 34,400	25	0.0025	0.0045	12.5	24.5
2	p.p.m.	75	0.0042	0.0024	21.0	12.0
E 1	$MgCO_3+CO_2$ for 1	25	0.0007	0.0054	3.5	27.0
2	hour	75	0.0009	0.0049	4.5	24.5
F 1	$CaCO_3+CO_2$ for 1	25	0.0004	0.0056	2.0	28.0
2	hour	75	0.0003	0.0058	1.5	29.0

A general survey of Table IV shows that sodium chloride and sea salt are the most effective precipitants of this type of colloidal silica, and that time is one of the chief factors in precipitation. Magnesium sulphate acts as a distinct stabilizer and this is probably due to the high concentration of this salt. The quantity of silica precipitated in 75 days varies little from that precipitated in the blank. It is fairly safe to conclude, therefore, that these two electrolytes are not effective precipitants of colloidal silica solutions containing 30 parts per million silica. A striking feature is the high concentration of silica that still remains in the filtrate

in each experiment, showing that even at the end of 75 days partial precipitation only had taken place. This result is in agreement with that of Zsigmondy [86] who states that silica solutions of one per cent. or less concentration are often stable for years and that they are coagulated immediately by very few electrolytes.

In order to determine the precipitating effect of the various electrolytes on more concentrated solutions of the colloidal silica 50-c.c. samples containing 500 parts per million silica were taken. To each sample was added electrolytes as before and in no case did precipitation occur at the time of addition of the salt.

On examining the sample at the end of 75 days it was seen that in A, which contained only colloidal silica, there was practically no indication of a precipitate, also, in C, which contained magnesium sulphate there was practically no indication of a precipitate. B, and D, which contained sodium chloride and sea salt respectively, showed a good precipitate of characteristic, flocculent, colloidal silica.

Formed by dialyzing a mixture of sodium silicate and hydrochloric acid.

Precipitation by electrolytes.—The investigation so far has dealt only with the precipitating effect of electrolytes up to the concentrations of those in sea water, and of sea water itself on dilute sodium silicate solutions and on dialyzed sodium silicate solutions containing only the colloidal silica that was formed by hydrolysis. The next step is the production of a silica hydrosol under different conditions, and the testing of the precipitating effect on it of various electrolytes.

Silica hydrosol may be prepared according to Graham's method, which is outlined by Zsigmondy.[87] The method consists of mixing 10-per cent. sodium silicate and 10-per cent. hydrochloric acid and dialyzing the mixture to free it from electrolytes. According to Mellor [88] the following reaction takes place:

$$Na_2SiO_3 + 2HCl \rightleftarrows H_2SiO_3 + 2NaCl.$$

[86] Zsigmondy, R., Spear, E. B., "Chemistry of Colloids," pp. 134–135, 1917.
[87] *Idem*, p. 134.
[88] Mellor, J. W., "Modern Inorganic Chemistry," p. 774, 1920.

It has not been definitely established whether the colloidal silica remains as silicic acid (H_2SiO_3) or whether the silicic acid breaks up according to the following equation:

$$H_2SiO_3 \rightleftarrows H_2O + SiO_2.$$

In this series of experiments the silica hydrosol was prepared by mixing water glass (specific gravity 1.0880) with an equal volume of 10 per cent. hydrochloric acid. The water glass was poured, with constant stirring, into the hydrochloric acid. The mixture was then dialyzed in order to free it from the hydrochloric acid and sodium chloride. The dialysis was considered complete when the solution gave no test for chloride with silver nitrate.

A portion of the silica hydrosol was analyzed and found to contain 8,310 parts per million silica. A portion of the hydrosol was then diluted 277 times, giving a silica hydrosol containing 30 parts per million silica. The chosen electrolytes were added to 50-c.c. samples of the hydrosol and the following results observed:

A 1, Blank, containing only colloidal silica.

B 1, Sodium chloride (34,400 parts per million). No evidence of a precipitate.

C 1, Magnesium sulphate (34,400 parts per million). No evidence of a precipitate.

D 1, Sea salt (34,400 parts per million). No evidence of a precipitate.

E 1, Magnesium carbonate, with carbon dioxide passed through solution for one hour. No evidence of a precipitate.

F 1, Calcium carbonate with carbon dioxide passed through the solution for one hour. No evidence of a precipitate.

These experiments were repeated and similar results obtained. The two sets were set away and examined periodically. At the end of 25 and 75 days respectively, they were filtered and the precipitates and filtrates analyzed. The results are given in Table V.

TABLE V.

EXPERIMENTS ON THE PRECIPITATION OF SILICA FROM DIALYZED SOLUTIONS OF COLLOIDAL SILICA CONTAINING 30 PARTS PER MILLION SILICA.

Exp.	Salt in Solution with Colloidal Silica.	Time in Days.	Gms. SiO_2 in Precipitate.	Gms. SiO_2 in Filtrate.	SiO_2 in Ppt. Recalculated to p.p.m. of Original Solution.	P.p.m. SiO_2 in Filtrate.
A 1	Blank	25	0.0003	0.0014	6	28
2	"	75	0.0006	0.0012	12	24
B 1	NaCl, 34,400 p.p.m.	25	0.0003	0.0012	6	24
2		75	0.0004	0.0013	8	26
C 1	$MgSO_4$, 34,400	25	0.0002	0.0014	4	28
2	p.p.m.	75	0.0003	0.0013	6	26
D 1	Sea salt 34,400	25	0.0005	0.0012	10	24
2	p.p.m.	75	0.0008	0.0010	16	20
E 1	$MgCO_2+CO_2$ for	25	0.0003	0.0014	6	28
2	one hour	75	0.0004	0.0018	8	36
F 1	$CaCO_2+CO_2$ for	25	0.0004	0.0012	8	24
2	one hour	75	0.0006	0.0014	12	28

A survey of Table V. shows that the colloidal silica formed when water glass is acidified with hydrochloric acid and dialyzed is very difficult to precipitate. Even at the end of 75 days as much as 20 parts per million remained in solution and in most cases the amount was much higher.

Sea salt appears to be the best precipitant of this type of colloidal silica, although the amount precipitated does not vary greatly from that obtained in the blank.

Magnesium bicarbonate and calcium bicarbonate do not appear to have any precipitating effect as the amount of silica thrown down is very little different from that shown in the blank. These electrolytes, however, show a considerable addition of silica in the filtrate, which is probably due to silica dissolved from the container. These results agree with those of Lovering, who found that magnesium bicarbonate and calcium bicarbonate were two of the best solvents of silica in nature.

This type of colloidal silica may be stabilized by suspended calcium carbonate, for according to Bancroft [89] colloidal silicic acid

[89] Bancroft, W. D., "Applied Colloid Chemistry," p. 220, 1921.

adsorbs lime from suspended calcium carbonate and thus acts as a peptizing agent. Consequently the protective influence of the calcium carbonate on the colloidal solution would tend to counteract any precipitating influence that the bicarbonate might have.

It was not to be expected that sodium chloride would have any precipitating effect on this type of colloidal silica because it was originally prepared in such a manner that hydrochloric acid and sodium chloride were in excess although these were later removed by dialysis. This neutral effect, however, does not hold for concentrated colloidal solutions, for with these coagulation, or even gelling, takes place if the concentration is high enough.

It is quite probable that this type of colloidal silica would be precipitated by sea water, if sufficient time was allowed. It would appear from a study of Table V. that any precipitation that had occurred was due to the combined effects of the electrolytes rather than to that of any single one.

The conclusions may be summarized as follows:

1. Sea salt acts with time as a precipitant of silica from silica hydrosols containing 30 parts per million silica and formed by dialyzing a mixture of water glass and hydrochloric acid.

2. Magnesium sulphate acts as a distinct stabilizer of this type of colloidal silica.

3. Sodium chloride, up to the end of 75 days, shows no precipitating effect.

4. Magnesium bicarbonate and calcium bicarbonate tend rather to dissolve more silica from the container than to precipitate the colloidal silica already in solution.

5. This type of colloidal silica is very difficult to coagulate by electrolytes such as are in the sea, but at least part of the silica is precipitated, providing sufficient time is allowed, showing that here, also, time is one of the most important factors in precipitation.

Precipitation by Calcium and Magnesium Bicarbonate.—Considerable work has been done on the precipitation of colloidal silica by carbon dioxide, calcium carbonate and calcium bicarbonate, and very contradictory results obtained. Church [90] found that

[90] Church, A. G., *Jour. Chem. Soc.*, 15, p. 107, 1862.

one milligram of finely powdered calcite in the bottom of a beaker, into which 100 c.c. of a 1 per cent. silica solution was poured, in ten minutes' time converted the silica into a gel so solid that the vessel could be inverted. Dean[91] prepared a colloidal silica solution from water glass and hydrochloric acid and purified it by dialysis until free from chlorides. To test the precipitating power of calcium carbonate and calcium bicarbonate and the effect of carbon dioxide on the silica hydrosols he took two samples. One sample was freed from carbon dioxide and the other was saturated with it. Ground calcite was added to both. The colloidal silica solution free from carbon dioxide remained stable for over a year, while that which had been saturated with it precipitated within an hour. Dean takes this result as evidence that carbon dioxide in the presence of calcium carbonate is a precipitant of silica hydrosols and that calcium carbonate in the absence of carbon dioxide is a remarkable stabilizer because the original silica hydrosol precepitated within a few weeks. He explains that the colloidal silica is not deposited by carbonic acid, as it is a weak electrolyte, but that it is deposited when carbonic acid comes in contact with calcium carbonate. This is due to the formation of calcium bicarbonate, which dissociates as shown below:

$$Ca(HCO_3)_2 \rightleftarrows Ca + 2HCO_3.$$

The divalent positive calcium ions so formed were believed to cause the precipitation of the negatively charged colloidal silica. He reconducted the experiments, using dolomites and calcareous shales, and obtained similar results.

In these experiments Dean does not state whether he analyzed the supernatant liquid in order to determine whether it still contained silica, and he does not state the concentration of the silica hydrosol. This is an important point since it cannot be assumed that electrolytes act in a similar manner on silica hydrosols of varying concentrations.

[91] Dean, R. S., *Amer. Jour. Sci.*, 45, p. 413, 1918; Cox, G. H., Dean, R. S., and Gottschalk, V. H., School of Mines and Metallurgy, University of Missouri, Bull. 2, vol. 3, p. 9, 1916.

Lovering [92] has shown that a dilute dialyzed silica solution made similarly to those used by Dean can retain considerable silica in solution in the presence of calcium bicarbonate, and he concludes that calcium bicarbonate and magnesium bicarbonate rarely act as precipitants in nature. He does find, however, that calcium bicarbonate is a precipitant of colloidal silica when the concentration of the solution is over 40,000 parts per million. Lovering's results are very similar to those shown in Experiments *E* and *F*, Table IV., but he does not mention the time factor.

The results of Experiments *E* and *F*, Table IV., show very conclusively that calcium and magnesium bicarbonate are not good precipitants of colloidal silica when the concentration of the silica is as low as 30 parts per million. It was decided, however, to perform a further series of experiments in order to see whether an explanation could be found for the very different results that have been cited above.

Solutions of colloidal silica of varying concentrations, formed by dialyzing a mixture of water glass and hydrochloric acid, were treated with magnesium carbonate, calcium carbonate and carbon dioxide. With the exception of the experiment in which carbon dioxide only was passed through a colloidal solution containing over 50,000 parts per million silica no precipitation occurred immediately. The colloidal silica solution in this case, however, gelled while the carbon dioxide was being passed through it, showing that at such high concentrations even carbon dioxide alone precipitates colloidal silica.

At the end of 60 days the colloidal solutions were filtered and the precipitates and filtrates analyzed. The results are given in Table VI.

The results in Table VI. show that concentration and time are two important factors in the precipitation of colloidal silica by electrolytes such as magnesium and calcium bicarbonate. Experiments 1 and 2 show that even after 60 days 26 and 29 parts per million silica remain in colloidal solution in the presence of calcium and magnesium bicarbonate. Experiments 3, 4, 5, and

[92] Lovering, T. S., ECON. GEOL., 18, pp. 537–538, 1923.

6, containing higher concentrations of colloidal silica, show a precipitate of silica at the end of 60 days, although here, also, from 27 to 44 parts per million are still in colloidal solution in the presence of calcium and magnesium bicarbonate, and at the time of commencing the experiments there was no evidence of precipitation. Experiments 1, 5, and 6 showed that passing carbon dioxide for one hour through the colloidal silica solutions to which the carbonate was added is just as effective as passing it through for three hours. Experiment 7 shows a relatively large proportion of silica still remaining in solution. In this case, passing carbon dioxide through the solution before adding ground calcite may have had some effect. It may be possible that carbon dioxide acts as a stabilizer at this concentration and that on adding ground calcite the resulting calcium bicarbonate has to overcome the stabilizing effect of the carbon dioxide, as well as the charge on the colloidal silica itself. Experiment 8 is a very

TABLE VI.

EXPERIMENTS ON THE PRECIPITATION OF COLLOIDAL SILICA SOLUTIONS BY CALCIUM BICARBONATE AND MAGNESIUM BICARBONATE.

Exp.	Colloidal Solution.	Reagent Added.	Results Obtained on Analysis 60 Days after Adding Reagent.		
			Gms. SiO_2 in Ppt.	Gms. SiO_2 in Filtrate.	P.p.m. SiO_2 in Filtrate.
1	100 c.c. dialyzed SiO_2, 30 p.p.m.	$CaCO_3+CO_2$ for 1 hr.	0.0005	0.0026	26
2	100 c.c. dialyzed SiO_2, 30 p.p.m.	$MgCO_3+CO_2$ for 1 hr.	0.0008	0.0029	29
3	100 c.c. dialyzed SiO_2, 60 p.p.m.	$CaCO_3+CO_2$ for 1 hr.	0.0034	0.0028	28
4	100 c.c. dialyzed SiO_2, 60 p.p.m.	$MgCO_3+CO_2$ for 1 hr.	0.0024	0.0044	44
5	50 c.c. dialyzed SiO_2, 150 p.p.m.	$CaCO_3+CO_2$ for 3 hrs.	0.0068	0.0013	27
6	50 c.c. dialyzed SiO_2, 150 p.p.m.	$CaCO_3+CO_2$ for 2 hrs.	0.0072	0.0014	28
7	100 c.c. dialyzed SiO_2, 150 p.p.m.	CO_2 for 3 hrs. ground calcite added.	0.0038	0.0118	118
8	100 c.c. dialyzed SiO_2, 10,000 p.p.m.	$MgCO_3+CO_2$ for 6 hrs.		0.0122	122

good illustration of the effect of magnesium bicarbonate on solutions of high concentration. When the magnesium carbonate and carbon dioxide were first added there was no indication of a precipitate, but at the end of 3 days an appreciable one appeared and it increased gradually in size during the time of experimentation. This result likely explains why Lovering obtained no precipitate upon adding calcium bicarbonate to 2 per cent. colloidal silica solution in 24 hours whereas on reconducting the experiment, using a 4 per cent. solution a heavy precipitate was obtained. It is quite probable that if Lovering had examined his 2 per cent. solution at the end of several days he would have seen distinct evidence of precipitation.

In summing up the results it may be said that even inert substances such as carbon dioxide and calcium carbonate precipitate colloidal silica from solution provided the concentration of the silica is sufficiently high. Calcium bicarbonate and magnesium bicarbonate are also very efficient precipitants in highly concentrated solutions but this precipitating power diminishes with the dilution. At dilutions such as exist in natural waters calcium and magnesium bicarbonate rarely act as precipitants of this type of colloidal silica, and if they do a long period of time is required to produce a result. These observations support the statement of Boydell,[93] who remarks on the conflicting statements regarding the stability of silica sols, particularly in regard to their stability with carbon dioxide, and states that this is probably due to variation in stability with concentration and possibly also to the presence of undetected protective agents.

Effect of Time and Concentration.—In order to illustrate more fully that time and concentration are two very important factors in the precipitation of colloidal silica by electrolytes such as are in the sea, a colloidal silica solution containing approximately 50,000 parts per million silica was prepared by dialyzing a mixture of water glass and hydrochloric acid. One hundred c.c. of this solution was divided into two 50-c.c. portions and to one of these portions sea salt in the proportion of 34,400 parts per mil-

[93] Boydell, H. C., *Trans. Inst. Min. and Met.*, p. 14, 1924.

lion was added. The other 50-c.c. portion was in turn divided into two parts. One part was made up to 50 c.c., giving a concentration of 25,000 parts per million silica, and to it was added also sea salt in the proportion of 34,400 parts per million. The remaining part was also made up to 50 c.c., divided into two equal portions, one of which was increased to 50 c.c., and sea salt added to it in the proportion of 34,400 parts per million, giving a concentration of 12,500 parts per million silica. This process was repeated until solutions containing 6,250, 3,125, 1,562, 781, 98, 49, and 25 parts per million silica were obtained and to each was added sea salt in the proportion of 34,400 parts per million. On addition of the sea salt the following results were observed in the various test tubes:

1. A heavy precipitate of colloidal silica formed at once in the colloidal solution containing 50,000 parts per million silica. The precipitate was very dense and it settled to the bottom of the test tube.

2. No precipitate formed immediately in the colloidal solution containing 25,000 parts per million silica but at the end of 6 hours a fairly heavy precipitate was noticed. The silica had separated out as a gel and filled the greater portion of the test tube.

3. No precipitate formed immediately in the colloidal solution containing 12,500 parts per million silica but at the end of 48 hours a precipitate could be seen.

4. No precipitate formed immediately in the colloidal solution containing 6,250 parts per million silica but at the end of 4 days some precipitation had occurred.

5. There was no evidence of a precipitate in any of the remaining eight test tubes at the end of 4 days.

Nineteen days after the experiment was started a slight precipitate was noticed in No. 6 while in No. 5 it was very clearly shown.

The set of solutions was set away and owing to the absence of the writers was not examined again for 200 days. Examination at the end of this time showed a precipitate in all the tubes, although in Nos. 11 and 12 it was not very large and could best be seen by agitating the tubes.

These experiments show very conclusively that the lower the concentration of a silica hydrosol, the greater the length of time required for its coagulation by electrolytes.

The only explanation that suggests itself is that, with time, the silica particles gradually concentrate toward the bottom of the tubes and when a definite concentration has been reached the electrolytes are able to bring about coagulation.

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(*To be concluded in next number.*)

A STUDY OF THE MAGNETITE OREBODY AT CORNWALL, PENNSYLVANIA.

W. H. CALLAHAN AND W. H. NEWHOUSE.

INTRODUCTION.

In this paper the writers give the results of a detailed study of the magnetite orebody at Cornwall, Pennsylvania.

One of the writers [1] was connected with development work at Cornwall, in the summer of 1926, during which time he had the opportunity to collect specimens which were later studied in the laboratory. The results obtained in the laboratory when considered with the field data appear to throw new light on the genesis of this interesting orebody.

Of particular interest is the fact that the contact metamorphic minerals are zonally arranged relative to the diabase intrusive. This fact together with the establishment of a sequence of mineral deposition strongly supports the idea that the source of the mineralizing solutions was the adjacent diabase intrusive.

GENERAL GEOLOGY.

The brief review of the general geology given in this paper has been taken from Spencer's [2] work.

To quote from him: [3]

> The different formations have a general east-west trend through all this region, and for several miles both east and west of Cornwall the older (Paleozoic) and newer (Mesozoic) formations are separated by an intrusive mass of diabase which has a width in outcrop of 1,400 to 2,900 feet. The mines lie just south of this diabase in an isolated area of limestone, the southern boundary of which is formed by overlapping Mesozoic beds.

[1] W. H. Callahan.

[2] A. C. Spencer, "Magnetite Deposits of the Cornwall Type in Pennsylvania," U. S. Geol. Surv. Bull. 359, pp. 7–29, 1908.

[3] *Op. cit.*, p. 17.

The rocks in the immediate vicinity of Cornwall are Paleozoic limestone and Mesozoic shales intruded by diabase which has mainly the nature of a sill and is only in part cross-cutting.

The general relations of the rocks and ore are shown in the accompanying generalized north-south cross section.

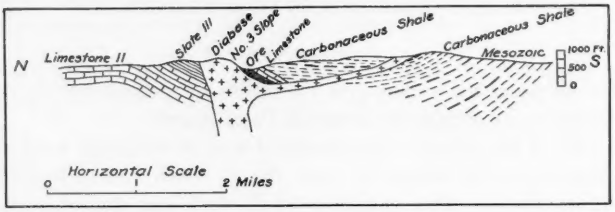

FIG. 1. Structure section through No. 3 slope. General relations from Spencer's maps and sections. Outline of the orebody as shown by prospecting and development work.

Limestone.—A Paleozoic limestone[4] forms the hanging wall of the orebody. In the hanging wall it is fine-grained, white to gray in color, and comparatively pure. Recrystallization has largely obliterated bedding, but enough has remained to show that the magnetite body lies or extends along the bedding; that is, replacement took place along the beds next to the sill. In common with the orebody, the limestone is remarkably free of those contact metamorphic minerals containing volatile constituents, although a few of the more common contact metamorphic silicates are sparingly represented. Recrystallized calcite is the main mineral of the rock, with minor amounts of augite, green biotite, and serpentine. Magnetite and pyrite appear in small masses filling in around calcite grains. Garnet, a typical contact metamorphic mineral, is so rare as to be a curiosity. None whatever was found in the orebody, but in the limestone, small scattered crystals appear which chemical tests and the index of refraction indicate are andradite. Numerous stringers of coarsely crystalline calcite traverse the limestone.

[4] Limestone II. (Cambro-Ordovician) of the Second Geological Survey of Pennsylvania.

Diabase.—At the contact with the orebody the diabase consists of a cryptocrystalline groundmass of feldspar, augite, and small evenly divided grains of magnetite; in this groundmass are set a few phenocrysts of plagioclase feldspar and augite. Olivine is present in rounded grains, surrounded by a halo of fine radiating augite crystals. Some of the olivine has been almost entirely altered to magnetite and serpentine, leaving only ghosts in the haloes.

Eight to ten feet from the contact olivine is rarely present and as the distance increases it disappears altogether. The texture in this decreasing olivine zone also changes from fine porphyritic to coarser ophitic as the distance increases from the contact. The minerals present in the typical ophitic textured diabase in the order of their abundance are, lath-shaped crystals of zoned andesine-labradorite feldspar, augite, green hornblende, brown biotite, micrographic intergrowths of orthoclase and quartz, irregular grains of magnetite and long needles of apatite. The magnetite has the appearance and general characteristics of deuteric magnetite described by Gillson.[5]

In some cases the apatite needles have a very definite geometrical pattern and replace the feldspar along its cleavage. The two minerals are undoubtedly later than the normal rock minerals and their association in this respect is interesting in view of the fact that the ores which are genetically related to the diabase are low in phosphorus.

Dikes a few inches in width composed of orthoclase, quartz, green hornblende, and calcite cut the diabase near its upper margin. These are considered to be a micro-pegmatitic phase of the diabase intrusive.

The diabase is remarkably fresh, only a little sericitization of the feldspar being observed near the contact.

Jointing is well-developed in the sill. Two systems were observed, one striking NE. and dipping steeply NW., and the other striking NW. and dipping steeply to the SW. Slickensided surfaces were observed only along the NW. striking system, and the

[5] J. L. Gillson, *Jour. Geol.*, vol. 35, p. 23, 1927.

other system is characterized by the development of pyrite, chalcopyrite, magnetite, green biotite, and small masses of albite and sericite. Some euhedral crystals of apophyllite were collected from seams in the diabase.

OREBODY.

Specimens were collected from a longitudinal vertical section of the orebody with a view to observing any changes in mineralogy from the hanging wall to the footwall. These specimens were not collected at regular intervals and are not considered to be free from the inherent defects of "grab" samples, but it is believed that they are amply representative for the conclusions arrived at in our study.

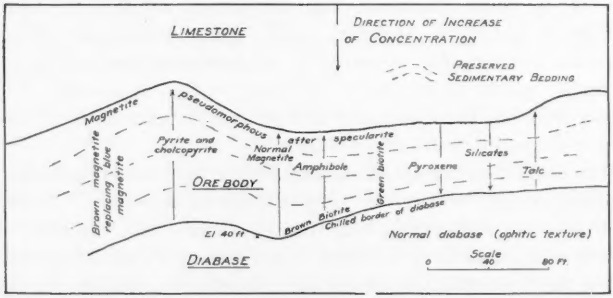

FIG. 2. Longitudinal vertical section along "C" west drifts, looking northwest, showing distribution of minerals.

The orebody lies immediately above the diabase and in the limestone, with both of which it has sharp, clean-cut contacts. One of its most striking features is the preservation of sedimentary structure, which is especially noteworthy when contrasted with the massive limestone comprising its hanging wall.

The ore in the lowest part of the orebody, that is, where it is closest to the diabase intrusive, is a hard variety with magnetite sparingly but evenly distributed through the rock. Bedding of the rock and cross-cutting veins of ore may be observed in this part of the orebody, and some masses of unreplaced limestone

form "horses" in the ore. The bedding is outlined by thin white, gray, and green bands containing varied amounts of calcite, silicates, and magnetite. In contrast to this in the upper part (Fig. 2) of the orebody (that is, closest to the limestone capping), the ore is softer and more concentrated. Not only do the iron oxides become more abundant farther from the intrusive but also pyrite and chalcopyrite become more abundant although still present only in small amounts. The upper part of the orebody near the contact with the limestone is characterized by the development of magnetite pseudomorphous after hematite although some of the hematite at the extreme border has not been replaced.

Gangue Minerals.—The gangue of the orebody where most concentrated is arranged in alternating dark green and gray bands from one-fourth to one-half an inch in thickness.

FIG. 3. Hand specimen of ore, showing the preserved sedimentary structure of the replaced beds. 4/5 actual size.

Bands such as these, which show in microscopic sections some fine indeterminate shaly material with silicates, are not present in

the hanging-wall limestone. This shows that shaly sedimentary bands were present in the limestone which was replaced by the ore but were not present in the limestone above the ore.

Green biotite is the main silicate gangue mineral present throughout the orebody, although tremolite and talc also occur. These latter two minerals are concentrated in the ore farthest from the diabase, *i.e.* near the limestone-ore contact. An intense replacement of brown biotite and augite occurs in a zone a few inches wide in the limestone adjacent to the diabase.

In general the silicates are most abundant near the diabase contact and decrease in amount toward the limestone hanging wall.

Ore Minerals.—A study of the polished sections prepared from the suite revealed the presence of the following metallic minerals: magnetite (some of which is lodestone), specularite, pyrite, chalcopyrite, and marcasite.

Two varieties of magnetite (?) are present throughout the orebody. The main one is a magnetite which has a bluish cast in polished sections, similar to that of the Port Henry, New York, and the New Jersey magnetites. The other one[6] is present in very small amount but is of widespread occurrence in the orebody. It has a brownish cast, is magnetic and slightly softer than the bluish one, which it replaces on the margins of grains and along octahedral directions. The writers believe that it is probably an oxidized form of magnetite like that described by Sosman and Posnjak,[7] and others.

It should be mentioned here that scattered grains of magnetite in the diabase are largely the bluish magnetite but many of them are peripherally replaced by the brownish variety.

Bluish magnetite is pseudomorphous after specularite in a zone a few feet in width in the upper part of the orebody, at its contact with the overlying limestone. Some of this bluish magnetite is in turn partly replaced by the brown.

Pyrite occurs as euhedral crystals and massive aggregates along the bedding in the ore and at times forms veins which transect the

[6] Described with other occurrences of the same mineral, ECON. GEOL., 22, pp. 629–632, 1927.

[7] *Jour. Wash. Acad. Sci.*, 15, pp. 329–342, 1925.

bedding. Where in contact with magnetite, the pyrite occasionally veins the crystals of it but more frequently fills in around the earlier crystals of the oxide. Towards the upper part of the orebody the pyrite and chalcopyrite increase in amount and the crystals of pyrite become larger.

Marcasite occurs in fine, elongated, parallel laths usually associated with chalcopyrite, although it has been observed to form at the contact of pyrite and magnetite. It occurs throughout the orebody with the exception of the top margin, where the magnetite pseudomorphic after specularite is found. It increases in amount with the chalcopyrite but evidence on the relative ages of the two minerals is inconclusive.

In the examination of the polished sections magnetite, pyrite, and chalcopyrite, with some residual fragments of tremolite, were found. These tremolite fragments are replaced by the metallic minerals along cleavage directions and in cross-cutting veinlets, which indicates that the tremolite is in part earlier than the metallic minerals.

Paragenesis

Pyroxene, biotite, actinolite, tremolite, and talc.
Specularite.
Magnetite blue (brown)?
Pyrite.
Chalcopyrite—marcasite?

SUMMARY OF MINERAL RELATIONS.

The silicate minerals are most concentrated toward the diabase intrusive and become less and less abundant toward the limestone hanging wall. Of these silicates, augite is most abundant near the diabase while tremolite is most abundant near the limestone. Very abundant, coarsely crystallized silicates do not occur, as so frequently happens in contact metamorphic deposits where the adjacent igneous rock is more siliceous.

Magnetite, pyrite, and chalcopyrite are all most abundant in that portion of the orebody which is farthest from the diabase. The specularite farthest from the diabase is less completely replaced by magnetite.

GENESIS.

Concerning the origin of the Cornwall deposit and other deposits of the same type in Pennsylvania, Spencer[8] says:

> They have been formed by the more or less complete metasomatic replacement of sedimentary rocks by iron minerals precipitated from heated solutions set into circulation by the invading diabase. The rocks which have been thus replaced are usually limestone, limy shales, or limestone conglomerates.

Although we lack the broad field studies of Spencer in this belt of deposits associated with diabase in Pennsylvania, from the study of the relationships at the Cornwall deposit described above, we see no reason to doubt his statement. In fact, the evidence which we have agrees strongly with the idea of the diabase being causally related.

The replacement appears to have taken place in the more shaly parts of the limestone, no doubt largely due to their position close to the intrusive. Since pure limestone is found nearby, there is a possibility that the ore has preferentially replaced the shaly beds. It would be interesting to examine closely the other deposits of this belt to see if a similar replacement of shaly beds has taken place.

The locus of origin of the solutions is an interesting problem. Although a positive statement can not be made on the question, the evidence favors an origin of the ore-bearing solutions in the immediately adjoining diabase. By referring to Fig. 2 it will be seen that the minerals are zonally arranged relative to the diabase sill. This it may be argued is a temperature effect of the still hot diabase on solutions which migrated up along the contact from a distant source and spread into the limestone forming the magnetite ore. No evidence of such a passageway for solutions has been found, for there is little alteration of the diabase at the contact. It would appear that the conduit for the solutions should be expected to be immediately at the diabase limestone contact if the zonal arrangement is to be accounted for. Since this is lacking, it seems logical to assume an origin of solutions close at hand.

[8] *Op. cit.*, p. 13.

The facts that the sulphides are later than the oxides, and the magnetite later than at least part of the silicates, and all these zonally arranged relative to the igneous rock, fits better into the explanation of the solutions coming from the nearby diabase.

It is believed that the best explanation of origin is that some time after the margins of the diabase sill began to crystallize the solutions were given off into the adjoining limestone. They effected little alteration in the marginal diabase, perhaps because, since they were given off by the crystallizing diabase, they would be of such a composition and temperature as to be about in equilibrium with the marginal diabase through which they passed toward the limestone. It will be recalled that this marginal diabase is much jointed and one set of joints is slightly mineralized.

Acknowledgment is made to Professors Waldemar Lindgren and J. L. Gillson for assistance in the laboratory, and to the staff of the Cornwall Division of the Bethlehem Mines Company for coöperation in the collection of the material. Thanks are also due the Bethlehem Mines Corporation for permission to publish.

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THE DETERMINATION OF ANISOTROPISM IN METALLIC MINERALS.[1]

EDWARD SAMPSON.

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In determining a metallic mineral, probably the most useful single test that may be applied is the test for anisotropism. In the laboratories of the U. S. Geological Survey and of Princeton University it has been found that the attachments for using polarized light are almost as useful and as much used in examining a polished section as in examining a thin section. The test for anisotropism should be the first test applied after a general inspection of the section, because it is both the easiest to make and the most instructive. It appears that this test has not been so generally applied as its usefulness would warrant. The purpose of this paper is to give a brief statement of the principles involved and the methods by which the tests are made, and to describe briefly apparatus with which effective work can be done. This paper contributes few new data, but is presented with the hope that it may prove of service to those who are not already familiar with

[1]Presented before the Society of Economic Geologists at Madison, Wisconsin, December, 1926.

Published by permission of the Director of the U. S. Geological Survey.

this important means of investigation.[2] The author wishes to acknowledge his indebtedness to A. W. Stickney for permission to publish Fig. 5, and to M. N. Short for critical reading of the manuscript and important suggestions.

PRINCIPLES INVOLVED.

Von M. Berek has contributed an excellent statement of the effects produced by polarized light to H. Schneiderhöhn's "Anleitung zur mikroskopischen Bestimmung und Untersuchtung von Erzen and Aufbereitungs-produkten besonders im auffallenden Licht." A clear statement of the principles may be found in Paul Drude's "Theory of Optics," which has been made readily available by the translation of Mann and Millikan. F. E. Wright has partly adapted the mathematical discussion of the principles to the special case presented to the student of ores in his paper "Polarized light in the study of ores and metals."[3]

The effects observed with polarized light may be briefly stated as follows: When polarized light is thrown perpendicularly onto a polished section of a metallic mineral a large part of it is reflected.[4] But before being reflected, this light has penetrated far enough to be affected by the atomic structure of the mineral. In the anisotropic minerals the principal effect of this penetration is to change the direction of the plane of polarization. The reflected light is still essentially plane-polarized, but the plane of polarization is in a different direction from that of the incident light. In other words, the plane of polarization of the reflected light has been rotated with respect to that of the incident light. If the analyzer is set at exactly 90° to the polarizer it will not be in a position to cause complete extinction and some light will be seen. With a nearly white mineral, for example manganite, a

[2] A paper by F. F. Osborne, on "Technique in the Investigation of Iron Ores," ECON. GEOL., vol. 23, pp. 442–450, 1928, deals in part with the use of polarized light applied to polished surfaces of ores.

[3] *Proc. Amer. Phil. Soc.*, vol. 58, pp. 401–447, 1919.

[4] In setting the polarizer, the common instruction is that the polarizer be set so that its plane of polarization is the same as that produced by reflection at the vertical illuminator. However, little, if any, change can be detected if the planes of polarization be at right angles instead of parallel. But if these planes are about 45° apart, serious disturbing effects are introduced.

faint gray will appear when the nicols are crossed, and this may be extinguished completely by rotating the analyzer to correspond with the rotation of the plane of polarization caused by the mineral. When such a colorless anistropic mineral is rotated with the stage it will be found that the plane of polarization is rotated first to the right and then to the left, with an intermediate position of no rotation. A complete rotation of the section under crossed nicols will show four bright positions at which the plane of polarization is rotated and four dark positions in which there is no rotation of the plane of polarization. The greatest amount of rotation caused by any mineral is probably between 5 and 8 degrees, but a rotation as great as 5 degrees is very uncommon.

Some minerals show colors under crossed nicols which bear no relation to the color of the mineral when seen with the analyzer out. These colors are not to be confused with the interference colors seen in the study of thin sections. Light which was plane-polarized before reflection may show after reflection some elliptical polarization, but the interference color that this would cause is of little effect—probably not more than a faint gray at most.

A few minerals will show in certain sections only two bright and two dark positions when viewed with the tube analyzer crossed. This is due to bi-absorption. The amount of light which is seen with crossed nicols depends on two factors: (*a*) the amount of rotation of the plane of polarization, and, (*b*) the amount of light reflected by the mineral. The amount of light reflected depends, in turn, upon the index of refraction and the index of absorption of the mineral. A decrease in either of these may offset the effect which would otherwise be produced by the rotation of the plane of polarization; and furthermore, if the decrease varies for light of different wave lengths, strong resultant colors will appear. From a combination of these factors, a strong rotation of the plane of polarization may be completely masked. However, if the Wright bi-quartz wedge plate be used the regular effects are observed; for with this plate actual rotation is the effective agent, not modified by the intensity of the reflected light.

For qualitative work, the most effective test is whether or not, with the nicols crossed or nearly so, the mineral changes intensity of color when the stage is turned. If the intensity changes, the mineral is anisotropic.

MANNER OF OBSERVATION.

Methods Available.—Anisotropism may be detected in three ways: (1) with the analyzer in the crossed position; (2) with the analyzer slightly rotated from the crossed position; and (3) by the use of a Wright bi-quartz wedge plate and cap nicol.

Analyzer Crossed.—This is the least sensitive of the three methods. As the stage is rotated, a strongly acting mineral will change from complete darkness to a very faint illumination. An analysis of the effects is given in Fig. 1, A.

Analyzer Turned.—If the analyzer be placed so that it is not exactly in the crossed position the anisotropic effect can be seen better, particularly when several contiguous grains of the mineral lie in the same field. When the analyzer is thus turned, the mineral, when in the four positions of no rotative effect, will be in extinction as if it were isotropic; but when in the four positions of greatest rotative effect, the mineral will be brighter or darker than it would have appeared had the analyzer not been turned, because the mineral by its rotative effect is adding to or subtracting from the effect of the turned analyzer. The advantage of this method of observation is similar to that obtained by using a gypsum plate with a petrographic microscope to secure a sensitive tint. The eye can better detect changes in the intensity of a moderate brightness than of almost complete darkness. Figure 1, B and C, shows the manner in which this method works.

In a section which shows several grains of a mineral, the effect of anisotropism is readily seen for one grain may be in the position of least illumination while its neighbor may be in the position of greatest brightness.

Wright bi-quartz wedge plate.—An effect similar to that caused by the granular aggregate is produced in a single grain by using

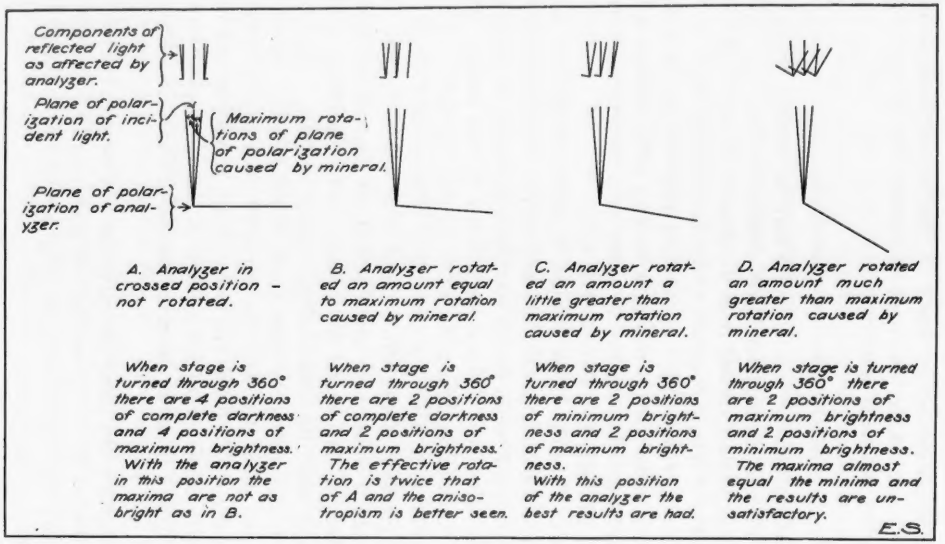
Components of reflected light as affected by analyzer.
Plane of polarization of incident light.
Maximum rotations of plane of polarization caused by mineral.
Plane of polarization of analyzer.
A. Analyzer in crossed position – not rotated.
When stage is turned through 360° there are 4 positions of complete darkness and 4 positions of maximum brightness. With the analyzer in this position the maxima are not as bright as in B.
B. Analyzer rotated an amount equal to maximum rotation caused by mineral.
When stage is turned through 360° there are 2 positions of complete darkness and 2 positions of maximum brightness. The effective rotation is twice that of A and the anisotropism is better seen.
C. Analyzer rotated an amount a little greater than maximum rotation caused by mineral.
When stage is turned through 360° there are 2 positions of minimum brightness and 2 positions of maximum brightness. With this position of the analyzer the best results are had.
D. Analyzer rotated an amount much greater than maximum rotation caused by mineral.
When stage is turned through 360° there are 2 positions of maximum brightness and 2 positions of minimum brightness. The maxima almost equal the minima and the results are unsatisfactory.
E.S.

FIG. 1. Diagrams showing maximum rotations of plane of polarization caused by mineral and the effects observed with analyzer in various positions. In each case the results are considered for the maximum left, zero, and maximum right rotation caused by the mineral.

a Wright bi-quartz wedge plate with the analyzer in the exactly crossed position. This compares two moderately bright fields.

The plate contains two sections of quartz out parallel to the base. One section is from a right hand crystal, the other from a left. They are mounted so that the line separating them is a medial line in the microscope field. Half of the plate rotates light to the right and half to the left. The combined quartz sections are ground to a wedge, so that the degree of rotation varies according to the thickness of the part of the plate used. The plate is used with a cap nicol. If light reflected up the microscope tube is plane-polarized, and the plane of polarization corresponds to the zero setting of the cap nicol, the two halves of

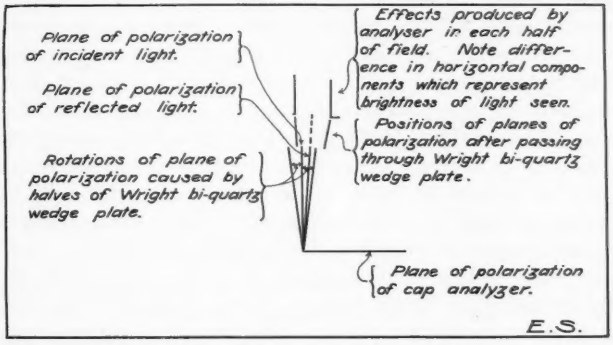
Plane of polarization of incident light.
Plane of polarization of reflected light.
Rotations of plane of polarization caused by halves of Wright bi-quartz wedge plate.
Effects produced by analyser in each half of field. Note difference in horizontal components which represent brightness of light seen.
Positions of planes of polarization after passing through Wright bi-quartz wedge plate.
Plane of polarization of cap analyzer.
E.S.

FIG. 2. Diagram showing manner of using Wright bi-quartz wedge plate for determining rotation of plane of polarization of reflected light by mineral.

the field will be equally illuminated. If, however, the reflected light has its plane of polarization turned from this zero position, as may be brought about by an anisotropic mineral, the intensity of illumination on opposite sides of the plate will differ according to whether the rotation caused by that side of the plate is the same as or opposite to that caused by the mineral (Fig. 2). If the cap nicol is now rotated an amount equal to the rotation caused by the mineral, the illumination will again be equal.

mum left, zero, and maximum right rotation caused by the mineral.

By this method the amount of rotation of the plane of polarization caused by the mineral may be measured quantitatively.[5] However, the principal use of the Wright bi-quartz wedge plate is for refined qualitative determinations, particularly when such determinations must be made on an isolated grain, with such a grain a slight change in the intensity of illumination is doubled by using the Wright plate, because the effect of the reflected light adds to the brightness of one side of the plate and detracts from that of the other side, according to whether the rotation caused by the mineral is the same as or opposite to the piece of rotating quartz in either half of the plate.

Importance of Strong Source of Light.—The effects observed either with or without the Wright plate may be much more easily seen by using a strong source of light. This seems an obvious improvement, but one which has not generally been put into effect. This is very important even for the qualitative tests, for if any confidence is to be placed in negative results, a very feeble effect must be observable. In the case of the most feebly acting minerals it is not sufficient merely to use the thick end of the Wright plate or, without the plate, to turn the analyzer far from the crossed position. For when these aids to brightness are resorted to, the change in brightness upon rotating the specimen is so small as compared to the total brightness that it may be imperceptible. By increasing greatly the intensity of the illumination the nicols may be almost exactly crossed and the change in brightness caused by rotating the specimen appears far greater. Although in each case the relative change may be the same, yet with a feeble light the absolute change in brightness is barely perceptible, whereas with a bright light the same relative change covers a larger absolute interval, and that through a range where the eye is much more sensitive. The conditions are somewhat analogous to trying to detect with the eye a 50 per cent. change in the intensity of infra red as compared to the same change of intensity in yellow.

[5] Sampson, Edward, "Note on the Determination of Anisotropism in Metallic Minerals," ECON. GEOL., vol. 18, pp. 775–777, 1923.

APPARATUS.

Requirements.—The writer is of the opinion that the best microscope for the study of polished sections should embody these features: (1) Slightly modified petrographic microscope of the erect type, and not the inverted metallographic arrangement in which much is sacrificed for ease in photography; (2) rotatable stage which may be raised and lowered; (3) polarizer attached to side of microscope tube and capable of precise setting; (4) tube analyzer which may be rotated and is movable a few degrees to the minus side of the zero setting. This fourth qualification is important, and is at present provided only on the more expensive microscopes. (5) The microscope should be designed so that a Wright ocular and Wright bi-quartz wedge may be attached. This is not essential, but is desirable for refined work. (6) A very strong source of light is of the greatest importance.

Apparatus Available.—There are three solutions to the problem of selecting suitable apparatus: first, adaptation of petrographic microscope; second, adaptation of inverted metallographic microscope; third, petrographic type of polished section microscope.

A petrographic microscope can be used for the study of polished sections by attaching a vertical illuminator to the bottom of the tube and using short mounted objectives. The principal objection to this apparatus is that, as the tube is at different heights with different sections and with different objectives, a remote concentrated source of light can not be used. The most simple arrangement for overcoming this difficulty is a lamp which is attached to the tube of the microscope. These are readily obtainable and may be attached to any style of petrographic microscope. The polarizer is ordinarily attached to the vertical illuminator. The analyzer is preferably in the tube but a cap nicol may be used. A tube analyzer should be rotatable and not fixed.

It is, however, readily possible to make the most inexpensive type of petrographic microscope suitable to refined work. In fact, the author has taken a microscope which was discarded as

unfit for undergraduate student use and made it usable with the addition only of a vertical illuminator, a cap nicol and a short mounted objective. The tube is held rigidly by a clamp supported by a laboratory standard, the stage being raised and lowered by the rack and pinion. The foot of the microscope and all substage equipment were removed to lighten the weight carried through the rack and pinion. The most inexpensive type of vertical illuminator was attached to the tube. The polarizer from the substage equipment was removed, and this, supported by another laboratory standard, was placed directly in front of the vertical illuminator.[6] The tube analyzer, which was not rotatable, was discarded and a cap nicol was attached. The source of light used was a strong arc with condensing lens, which is described later (see Fig. 3). Any strong concentrated source of light is suitable, and when the apparatus is once set up it remains adjusted, for the microscope stage and cap nicol are the only movable parts.

For refined work satisfactory results have been obtained by equipping an inverted microscope, of the type used for photography, so that polarized light is transmitted. This requires a polarizer between the light source and the microscope, and a cap nicol at the ocular tube. It should be noted that the analyzer should be attached to the tube used for photography, for the reflection by the prism attached to the tube for ordinary visual use causes serious disturbing effects.

In adapting a microscope for such work at the U. S. Geological Survey, a Bausch & Lomb inverted microscope, model GSA–IL9, was used.[7] The analyzer used was taken from a petrographic microscope. This was mounted on the stand for the collimating lens by attaching to this stand a plate with a sleeve into which fits the cylindrical mounting of the prism. The collimating lens

[6] The polarizer should be set so that the plane of polarization is in the same direction as that produced by the reflector of the vertical illuminator. Fairly satisfactory results can be obtained, however, by using a stationary analyzer and rotating the polarizer.

[7] This model has been superseded by an improved model, but will serve to illustrate how an adaptation may be made. The microscope is equipped with a ribbon-filament lamp.

was found not to be necessary. For the analyzer a Bausch & Lomb Wright ocular, designed for the bi-quartz wedge plate, and cap nicol of the same petrographic microscope were used. This accessory fits exactly the ocular tube of the metallographic microscope. This is, to be sure, a make-shift arrangement, but it is satisfactory. The photographs, Figs. 3 and 4, were taken with

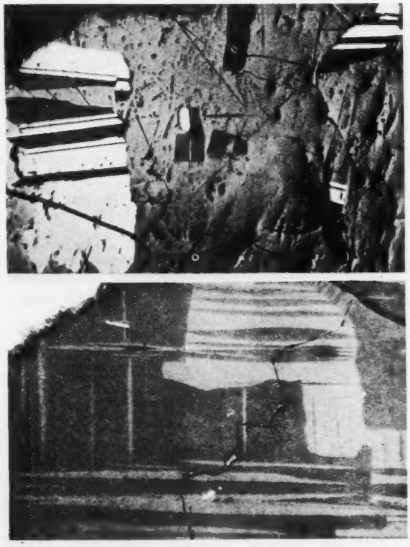

FIG. 3. Marcasite, showing polysynthetic twinning, in pyrite. Nicols nearly crossed. From material collected by A. W. Stickney and studied by him in the laboratories of the U. S. Geological Survey. This plate also illustrates that an imperfect polish does not interfere with clear-cut qualitative results. × 60.

FIG. 4. Twinning in chalcopyrite from Bass Prospect, Grand Canyon, Arizona. Grain of pyrite in upper left corner. Nicols nearly crossed. Specimen unetched. × 150.

this microscope. With other makes of microscopes, the problem will have to be solved in placing the polarizer differently, but

some make of Wright eyepiece will probably be found to be the most satisfactory for the analyzer, and with this the bi-quartz plate may be used.

The most important improvement would be to get the polarizer in the position where the beam of light is most concentrated, so that the smallest possible prism may serve. In the microscope above described this would be as close to the microscope as possible. Another important consideration is to get a cap nicol with the most accurate possible graduations (preferably a Vernier), so that the analyzer may be set with great precision. For qualitative work it is necessary to have a mechanical slow-motion screw arrangement to permit the delicate setting.

Microscopes especially designed for the study of polished sections with polarized light are available on the market and are much more satisfactory than equipment previously available. A setup of apparatus has been worked out by Dr. Willard B. Jewell and the writer which, although it embodies only simple changes, is so extremely convenient to operate, and so highly efficient, that a brief description is given.

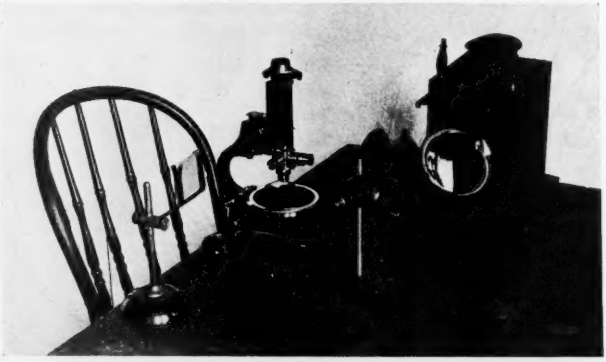

FIG. 5. Arrangement of equipment for visual study with reflected polarized light. The stand holding the ground glass screen ordinarily placed in front of the polarizer has been moved out of position to the left.

The general arrangement is shown in Fig. 5. Several features are to be noted. A powerful arc lamp with appropriate condensing system is used. In this case, the lamp from an old stereopticon was found suitable. The large collecting lens was made by the re-arrangement of several old lenses to form a double convex system. It forms a concentrated beam of light which is a very flat cone. This beam is twice reflected at right angles into the collimating lens by a pair of mirrors. This stand of mirrors and collimating lens is furnished by Leitz and is very useful. The setting of the mirrors to give a horizontal right angle is readily made. The lower mirror is movable about two axes, and by it the light may be centered.

The large arc employed gives a very strong light, and it is desirable not to have it in direct line of vision while using the microscope. A clockwork feed is not necessary, as the carbons will burn for over 10 minutes without adjustment. Furthermore, the position of the arc is such that it is in comfortable reach while seated at the microscope. Also, the equipment is mounted on a very low table which greatly lessens the fatigue of long observation. The arc housing, collecting lens, and collimating lens stand are screwed fast to the table. The microscope is movable so as to permit slight adjustment, and it is found that this causes no inconvenience.

For photographic work a vertical camera stand may be used.

Results Obtainable.—Any of the equipment described in this paper, used with a powerful light, will determine anisotropism in the metallic minerals with the greatest ease. Minerals which produce a very small rotation may be tested with confidence, and it appears likely that nearly all metallic minerals, other than amorphous and isometric minerals, should give an observable qualitative effect.

Examples of results which may be obtained are shown in Figs. 4 and 5.

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PRINCETON, N. J.

SOME COVELLITE–CHALCOCITE RELATIONSHIPS.[1]

ALAN M. BATEMAN.

A LITTLE over two years ago, while investigating some characteristics of the mineral chalcocite, I happened to heat some specimens to attempt to bring out diagnostic structures in the chalcocite, and found that covellite inclosed in the chalcocite disappeared upon heating. I then recalled that a year or so earlier A. C. Spencer showed me some specimens of bornite-chalcocite intergrowths with which he had been experimenting and found that the application of heat caused the bornite to disappear and that annealing appeared to bring back the intergrowths.[2] This, Dr. Spencer interpreted as indicating that solid solution had taken place upon heating, and that the bornite-chalcocite intergrowths had probably been formed originally by unmixing.

This finding stimulated the writer to examine further his intergrowths of covellite and chalcocite and to determine, if possible, if they also had been formed by unmixing from solid solutions. It was hoped that, among other things, the diverse interpretations previously given by different investigators to explain certain peculiar microscopic relationships between covellite and chalcocite might be clarified. In particular, information was desired as to whether the lath-like crystals of covellite in chalcocite really indicate replacement, as is usually interpreted, or unmixing from solid solutions. Also it was hoped that more precise information might be yielded regarding the primary (hypogene) or secondary (supergene) origin of certain doubtful chalcocites, and the genesis of the deposits that contain them. Experiments carried on show that natural covellite is readily absorbed in chalcocite upon heat-

[1] Presented before the Society of Economic Geologists; New York Meeting, Dec., 1928.

[2] Verbal communication regarding incomplete and unpublished experiments conducted at the U. S. Geological Survey, Washington.

ing at low temperatures; that solid solution takes place at relatively low temperatures; that isometric chalcocite is produced; and that unmixing of covellite and chalcocite can be induced by annealing. The conclusions that may be drawn from these findings will be discussed further on.

Subsequently, Wandke [3] published the results of his experiments on bornite-chalcocite intergrowths, as well as mixtures of some other minerals, and showed that bornite and chalcocite intergrowths upon heating tended to form a homogeneous substance. More carefully controlled experiments by Schwartz [4] checked Wandke's findings and established that bornite and chalcocite form solid solutions at temperatures of from 175–225° C. and that they break down again upon slow cooling into bornite and chalcocite. Schwartz has also shown [5] that cubanite is formed by transformation from a solid solution in chalcopyrite. Intergrowths of other minerals also have been shown to form solid solutions upon heating and to unmix upon slow cooling. For example, Ramdohr [6] in careful experiments has mixed and unmixed intergrowths of magnetite and ilmenite and hematite and ilmenite. Unmixing from solid solution has also been frequently advanced as an explanation of certain other mineral mixtures such as bornite and chalcopyrite intergrowths,[7] chalcopyrite specks in sphalerite,[8] and other mineral mixtures.

It is thus evident that the formation of some mineral intergrowths by unmixing from solid solution is now established. Consequently, the recording of the similar action of covellite and

[3] Wandke, A., "Molecular Migration and Mineral Transformation," ECON. GEOL., vol. 21, pp. 166–171, 1926.

[4] Schwartz, G. M., "Experiments Bearing on Bornite-Chalcocite Intergrowths," ECON. GEOL., vol. 23, pp. 381–397, 1928.

[5] Schwartz, G. M., "Intergrowths of Chalcopyrite and Cubanite," ECON. GEOL., vol. 22, pp. 44–61, 1927.

[6] Ramdohr, Paul, "Beobachtungen an Magnetit, Ilmenit, Eisenglanz und Ueberlegungen über das System FeO, Fe_2O_3, TiO_2," *Neues Jahrb. f. Min.*, Beil. Bd. 54, pp. 320–379, 1926.

[7] Van der Veen, "Mineragraphy and Ore Deposition," pp. 24, 47, The Hague, 1928; Wandke, *op. cit.*, p. 169.

[8] Schneiderhöhn, H., "Mikroskopischen Bestimmung und Untersuchung von Erzen," Berlin, 1922; Van der Veen, *op. cit.*

chalcocite contributes nothing new in principle. However, it does establish that another pair of minerals originate by unmixing from solid solution and that these give rise to microscopic structures that have commonly been interpreted previously to indicate replacement. Other interesting features in connection with heating effects upon covellite-chacocite mixtures are the low temperatures at which solid solution takes place, the nature of the changes, and the change in the symmetry of the chalcocite.

THE MATERIALS.

Two modes of occurrence of covellite associated with chalcocite are well known to those who have studied copper ores under the microscope. One is the familiar secondary or supergene covellite in which this mineral occurs as veinlets traversing other sulphides, as rims surrounding other mineral grains, or as irregular areas of feathery covellite encroaching boldly upon other sulphides. This mode of occurrence resembles that of supergene chalcocite; the two minerals may occur exclusive of each other or intermingled. Examples of these relationships are to be found in most deposits containing copper minerals that have undergone secondary enrichment and there is general agreement that such covellite is a secondary product that has replaced other sulphides.

In the other mode of occurrence the covellite is inclosed in chalcocite in the form of acicular, feathery or lath-like crystals, resembling phenocrysts of feldspar in an andesite porphyry. Less commonly, the covellite grains are shapeless. The covellite laths are usually of small size and may be sparingly scattered in the chalcocite or so abundant as to form a felted mass. This type of covellite is common in the ores of Kennecott, Alaska, and Magma, Arizona, and is frequently met with in other ores. An illustration of it may be seen in Fig. 1.

Under the microscope, in plane reflected light, the laths of covellite range in color from white to a beautiful deep blue, depending upon the orientation of the crystals on the polished surface. The white color is confusing to one who has not examined covellite under polarized light because of its close resemblance to

chalcocite. Under crossed nicols "pleochroism" is pronounced; the covellite laths take on brilliant red, yellow, and pink colors which change upon rotation of the stage. They extinguish four times in a complete rotation, parallel to the cross-hairs, and are most brilliant at 45 degrees to the cross-hairs. The inclosing

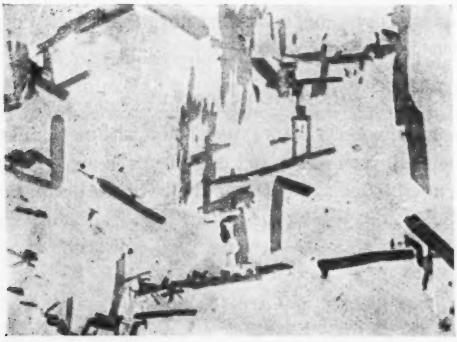

FIG. 1. Lath-like crystals of covellite (dark) inclosed in chalcocite (gray-white). Covellite laths are oriented along parting planes in the chalcocite. Kennecott, Alaska. ×80.

chalcocite, under crossed nicols, remains dark during a rotation of the stage if it is the high-temperature isometric form, and shows only slight change of color if it is the low-temperature orthorhombic variety. Consequently, there is a striking color contrast between the covellite and chalcocite which enables the two minerals to be distinguished at a glance. Even the slightest thread of covellite in the chalcocite, visible only under highest magnifications, stands out under crossed nicols in brilliant contrast to the sombre chalcocite. It is this variety of covellite that has given rise to difference of opinion as to its origin. Commonly it has been considered to indicate replacement of chalcocite by covellite, and the covellite has been interpreted as supergene; some investigators have considered that the covellite and chalcocite were deposited simultaneously and were either of supergene or hypogene origin.

This type of covellite was chosen for experimentation. It will be shown that the covellite laths disappear upon gentle heating; the covellite merges with the chalcocite and under crossed nicols not a vestige of the startlingly brilliant covellite can be discerned; only the dark field of isometric chalcocite may be seen. The determination that the covellite disappears is thus simple by the use of polarized light, and admits of not the slightest doubt of the presence or absence of covellite.

HEATING EXPERIMENTS.

In the earlier experiments polished specimens were simply heated over a Bunsen flame and cooled in the air. Examination under the microscope showed that the covellite disappeared completely or incompletely depending upon the amount of heating. Later, an electric oven was procured, with an automatic temperature control, a temperature-regulating device, and a mercury thermometer. Any desired temperature could be maintained for any desired length of time. At first, temperatures around 200° C. were used over a period of several days. Subsequently, lower temperatures and shorter intervals of time were used. Polished surfaces were cut in triplicates, one for examination and preserval of the original character, one for heating and examination, and the third for slow annealing. Thus comparison could be made between the same material treated under different conditions. A great many specimens were treated at different temperatures and over different periods of time. At first the specimens were heated in a bath free from oxygen, but check specimens given parallel treatment without such precautions showed that isolation from air was unnecessary. Consequently all subsequent heat treatments were carried on in an air bath. The specimens upon removal from the oven were allowed to cool in the air for a few seconds and were then examined under the microscope. It was found unnecessary to quench them. Subsequently they were rubbed lightly by hand upon a buffing chamois to remove surface tarnish, and re-examined. Specimens from Kennecott, Alaska, and Magma, Arizona, were used for most of the tests.

RESULTS OF EXPERIMENTS.

Effect of Heating.—A specimen of chalcocite containing lath-like crystals of covellite (Fig. 1) was heated at 110° for three hours. The covellite disappeared and a homogeneous substance resulted. The latter gives all the microchemical and physical tests for chalcocite. Even the color is that of ordinary chalcocite; there is no evidence under the microscope of a bluish tint such as is characteristic of "blue chalcocite." It is clear that the covellite has gone into solid solution in the chalcocite. No trace of covellite could be discerned by the delicate test under crossed nicols with reflected light. The substance is isotropic under crossed nicols, indicating that it is the isometric form of chalcocite. But

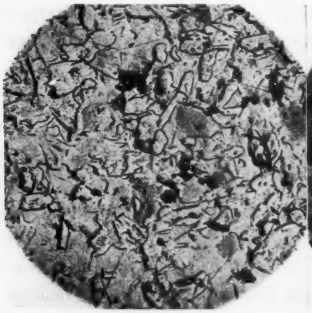

FIG. 2.

FIG. 3.

FIG. 2. Specimen of chalcocite with inclusions of covellite, after heating but not repolished. All lath-like inclusions of covellite have disappeared; residual remnants (dark gray) of larger irregular grains of covellite still remain. Areas in relief represent positions of former covellite laths. ×40.

FIG. 3. Another specimen of chalcocite and covellite after heating. Areas in relief were formerly covellite but are now chalcocite. Original positions of covellite are thus shown. Faint darker areas are residual covellite grains only partly absorbed in chalcocite. ×80.

a surprising feature of the heated surface is that it possesses noteworthy relief; the area of each former covellite lath now stands

up in relief, as is shown in Fig. 2. Thus the position and outline of each former covellite grain is sharply marked out. One might think that the covellite laths are still present, were it not that their areas are now occupied by chalcocite, which lacks the covellite color and reacts microchemically like chalcocite. Etching with HNO_3 over former boundaries between the two minerals gives the same reaction on both sides, but those parts which formerly were covellite yield a finer etch pattern.[9] Slight repolishing causes the relief to disappear, and then one cannot tell which parts were formerly covellite. But if this repolished surface is again etched, the former covellite areas become evident by the finer etch structure produced in them. These relief features show that areas which before heating were covellite have become chalcocite, or rather a solid solution of covellite in chalcocite. Though it is the covellite that has disappeared, the change upon heating was such that chalcocite has taken the place of the covellite.

The specimen described and pictured above is only one of many similar tests on specimens containing (by estimate) from 10 to 30 per cent. of covellite. Different results were obtained on specimens with a larger percentage of covellite or with different temperatures or length of heating period. To describe them all is unnecessary repetition. A few interesting features may, however, be noted.

Several specimens when heated showed that the covellite disappeared and its place was taken by chalcocite, except for a narrow rim, microscopic in size, around the margins of the former covellite laths. Apparently, for some reason not understood, the outer borders of the covellite resisted change. Under crossed nicols the brilliantly colored rectangular skeleton outlines of covellite mark the former position of the covellite laths.

Specimens in which solid solution was incomplete show laths with covellite centers whose margins are frayed and indistinct where they merge into chalcocite. Large grains of covellite commonly show this frayed appearance (see Fig. 3) where the chalcocite encroaches upon the covellite. The covellite remnants resemble residual nuclei of replacement.

[9] It should be remembered that covellite is negative to HNO_3.

One specimen with predominant covellite and a few small areas of chalcocite into which covellite laths projected, was heated to see if the chalcocite in the midst of covellite would be absorbed into the covellite and thus reverse the process. The projecting ends of covellite, upon heating, became absorbed by the small area of chalcocite, and the remaining parts of the covellite laths were unaffected. The small areas of chalcocite apparently absorbed all the covellite that they could contain. It is thus clear that the solid solution takes place in only one direction, *i.e.* the covellite passes into chalcocite but chalcocite does not ordinarily change into covellite, otherwise the small areas of chalcocite inclosed by covellite would have passed into covellite. Invariably, even though the proportion of chalcocite to covellite is very small, the former absorbs surrounding covellite to its capacity. In such specimens, areas of covellite where no chalcocite is present were unaffected by heating at the temperatures used; also specimens of pure covellite were unaffected by temperatures below 200° C. Specimens containing supergene covellite and chalcocite from Bingham, Utah, and Ely, Nevada, also were heated and solid solutions were formed between the two minerals.

Temperatures.—A surprising feature of the heat treatment of covellite-chalcocite mixtures is the low temperature at which solid solution takes place. After many tests at different temperatures and over different periods of time, it was found that temperatures over 150° C. were unnecessary and that a few hours sufficed as well as several days. With many specimens containing from 10 to 20 per cent. of covellite, solid solution took place at 115° C. in 1½ to 2½ hours. One specimen with about 20 per cent. covellite required only one hour at 120°. Another specimen with about 10 to 15 per cent. of covellite when heated for 1½ hours at 50° C. showed no change whatever, but complete solid solution took place in the same specimen when it was heated at 75° for 3 hours. These temperatures are even lower than those obtained by Posnjak, Allen, and Merwin,[10] who brought about solid solution

[10] Posnjak, Allen and Merwin, "The Sulphides of Copper," ECON. GEOL., vol. 10, pp. 491–535, 1915.

of covellite in chalcocite by heating compressed powders of artificial and natural minerals.

Effects upon Chalcocite.—It has been shown by Posnjak, Allen and Merwin [11] that chalcocite has two forms; an isometric form is produced above 91° C. which passes into an orthorhombic form below that temperature. Below 91° C. only the orthorhombic form is produced. They also found that chalcocite may contain covellite in solid solution and if the amount of covellite exceeds 8 per cent., inversion is prevented and chalcocite formed above 91° C. will remain isometric at lower temperatures. Consequently, if solid solution is induced in natural covellite-chalcocite mixtures by heating at temperatures above 91° C., isometric chalcocite should result.

Examination of the heated specimens shows that this has taken place. The chalcocite, in all cases where the admixed covellite has been estimated at 10 per cent. or greater, has been found after heating and rapid cooling to be isometric and not orthorhombic. The symmetry of the chalcocite was determined in each case by the use of polarized reflected light, supplemented by structures developed with etching. The former method, however, appears entirely reliable if precise apparatus is used. Under crossed nicols, the isometric chalcocite remains evenly dark during a complete rotation of the stage, showing that it is isotropic; the orthorhombic chalcocite, being anisotropic, displays faint "pleochroism," with two dark and two bright positions during a complete rotation of the stage. The determinations may be checked by means of the bright bi-quartz wedge.[12] The apparatus and methods for this determination are those used in this laboratory and recently described by F. F. Osborne.[13]

As many of the specimens used in the experiments came from Kennecott, Alaska,[14] both isometric and orthorhombic chalcocite were present before heating.

[11] *Idem.*

[12] F. E. Wright, "Polarized Light in the Study of Ores and Metals," *Proc. Amer. Phil. Soc.*, p. 401, 1919.

[13] Osborne, F. F., "Technique in the Investigation of Iron Ores," ECON. GEOL., vol. 23, pp. 442–450, June–July, 1928.

[14] It has previously been shown that in the Kennecott ores there is both ortho-

When covellite was made to go into solid solution with orthorhombic chalcocite, isometric chalcocite was formed. The one specimen previously mentioned as being heated for 3 hours at 75 degrees was orthorhombic chalcocite from Kennecott. Although complete absorption of the covellite took place at this temperature, the cooled product was orthorhombic chalcocite. However, when this same specimen was reheated for one hour at 100° C., the orthorhombic chalcocite became changed to isometric. Orthorhombic chalcocite specimens from Butte and Bristol were examined immediately upon removal from the oven, and while still hot were seen to be isometric but, after cooling, the chalcocite again passed to the orthorhombic form.

Annealing.—Attempts to unmix covellite and chalcocite from solid solutions by slow cooling were not very satisfactory. Cooling was produced by 10 degree drops in temperature from 100° C. to room temperature over periods of from one day to one week. Some specimens were placed in a refrigerator and subjected to temperatures below freezing for 24 hours. Most of the specimens showed no change; three of them showed a little unmixed covellite. In each case the covellite was in the form of small lath-like crystals of microscopic size. The new covellite shreds mostly formed irrespective of the position of the previous covellite laths; many cut directly across the ghost-like outlines of the former covellite grains. Their longer axes, as shown by extinction under crossed nicols, are aligned in triangular pattern. In one specimen from Kennecott, many small covellite crystals formed entirely in the old covellite positions but in haphazard orientation. The new laths are visible under crossed nicols but cannot be photographed.

DISCUSSION OF RESULTS.

Just what conclusions can be drawn from the results discussed, and what significance can be attached to them to help elucidate the problems of the origin of ore deposits? It must be admitted

rhombic and isometric chalcocite. See Bateman, Alan M, and McLaughlin, D. H., "Geology of the Ore Deposits of Kennecott, Alaska," ECON. GEOL., vol. 15, pp. 1–80, 1920.

that the conclusions that may be drawn are few and that some of these must await the outcome of further work now in progress.

It has long been thought that solid solution of covellite and chalcocite occurs, and in 1915 Posnjak, Allen and Merwin definitely established that it takes place in artificial and natural sulphide powders.[15] They also found that two specimens of Kennecott chalcocite contained over 8 per cent. covellite in solid solution.

The experiments described above likewise demonstrate that solid solution takes place with comparative ease in natural mineral aggregates of covellite and chalcocite, and a homogeneous-appearing isometric chalcocite or chalcocite with covellite in solid solution results. Slow cooling also brings about partial unmixing of the solid solutions into covellite and chalcocite. It appears likely, therefore, that natural chalcocite with inclosed crystals of covellite of the character described (excluding the low temperature supergene covellite) has been formed by unmixing under natural conditions. If this is true, such ores must have been formed at temperatures higher than those that prevail under conditions of supergene enrichment.

Significance of Natural Solid Solutions.—That solid solution does not take place at normal temperatures is indicated by the experimental results. Likewise the absence of features typical of covellite that has been partly absorbed into chalcocite shows that ordinary supergene covellite and chalcocite have not formed solid solution under natural near-surface conditions. Consequently, the occurrence of natural solid solutions of chalcocite and covellite, such as the isometric chalcocite with inclosed covellite of Kennecott,[16] shows that they must have been formed at elevated temperatures. Such elevated temperatures may have prevailed either at the time of formation of the minerals or at some time subsequent to the formation of the ore deposits. If the elevation of temperature had taken place subsequent to the formation of the

[15] *Op. cit.*

[16] It must be remembered that natural isometric chalcocite would not exist at normal temperatures if it did not contain covellite in solution; otherwise it would revert to the orthorhombic form.

deposit, and induced solid solution between pre-existing chalcocite and covellite, then evidence of this should be seen in the frayed character of the remaining covellite. Such evidence is lacking. Therefore it is inferred that the temperature necessary to induce solid solution in nature must have existed at the time of formation of the ores. Consequently, the natural occurrence of such solid solutions is an indication of hypogene origin. In the case of the Kennecott ores, it adds another argument to those previously advanced [17] that the Kennecott chalcocite is primary or hypogene. Likewise some of the chalcocite from the Magma mine appears to be primary.

Disappearance of Covellite.—The disappearance of covellite is, in the writer's opinion, unquestionably due to the formation of a solid solution between it and chalcocite. The question might be raised that the covellite has been converted into chalcocite by driving off an atom of sulphur from the covellite. But this does not appear likely, because: (*a*) the temperatures used were lower than those at which sulphur is driven off from covellite; (*b*) no evidence of sulphur was seen; (*c*) pure covellite subjected to similar heat treatment was not affected; (*d*) the change took place only where covellite was in actual contact with chalcocite.

Mechanism of Change.—The mechanism of the change from covellite to chalcocite raises some interesting problems. Does the so-called solid solution take place by an interpenetration of the lattices of covellite and chalcocite, or by migration of atoms of copper, or of sulphur? No answer can be given to this as yet. It is hoped that work now in progress may offer a solution.

The simplest explanation would be to assume that activation by heat causes an atom of sulphur to migrate out of the covellite into the chalcocite lattice, thus bringing about the change of covellite (CuS) to chalcocite (Cu_2S). Posnjak, Allen and Merwin [18] have already shown that artificial and natural chalcocite contain excess sulphur. Evidently, the absorption of covellite, or of sul-

[17] Bateman, Alan M., and McLaughlin, D. H., "Geology of the Ore Deposits of Kennecott, Alaska," ECON. GEOL., vol. 15, pp. 1–80, 1920.

[18] *Op. cit.*

phur, in chalcocite, is not dependent upon the inversion of chalcocite from the orthorhombic to the isometric form, since solid solution has been made to take place at temperatures below that of the inversion temperature of chalcocite.

A suitable explanation must also be sought as to why the change appears to proceed only from covellite into chalcocite and not from chalcocite into covellite. It has been pointed out that in specimens of predominant covellite with only small particles of included chalcocite, the latter upon being heated are not absorbed into the larger volume of covellite, but the small mass of chalcocite absorbs covellite to its capacity and then no further change takes place upon continued heating.

Significance of Relief.—It has been pointed out that upon heating, the areas that were originally covellite stand out upon the polished surfaces in marked relief. This must indicate that a change in volume takes place when the covellite becomes chalcocite. But, contrary to what one would expect, the volume change is an increase rather than a decrease. The significance of this is not as yet understood.

Unmixing.—In contrast with the ease with which solid solution is brought about, the difficulty of obtaining unmixing of covellite from the solid solution is rather surprising. The few cases so far obtained seem fortuitous; the repetition of experiments upon similar material has not as yet yielded sustained results. The controls are, therefore, not known. There is thus raised another problem as to why unmixing cannot readily be induced and what significance this may have with respect to the process of solid solution. It is of course realized that the velocity of the unmixing will be a maximum at a certain temperature, and this temperature can only be determined by experiment. It may have happened that the three cases of unmixing were obtained largely by accident, because in the annealing the maximum temperature of velocity of change may by chance have existed for sufficient time to allow some unmixing to occur.

The obtaining in a few cases, however, of unmixed covellite laths, even though they are of minute microscopic size, shows that

covellite does unmix from a solid solution with chalcocite. The similarity of these minute covellite laths to the larger laths inclosed in chalcocite (Fig. 1), and the fact that the latter commonly lie along parting planes in the chalcocite, suggest that they also formed by unmixing from solid solution with chalcocite. This, however, cannot be considered to be proved as yet. The similarity, also in the appearance of the covellite lath-like inclusions as compared with the unmixed products obtained by Ramdohr [19] and with those obtained from unmixed alloys, is a further suggestion that the lath-like covellite inclusions of the Kennecott ores are due to unmixing. If this is true, replacement need not be invoked to explain this type of texture.

Application to Kennecott Ores.—The experimental and microscopic study suggests the possibility that, for the major part, the Kennecott chalcocite was originally deposited,[20] perhaps as a colloid, with a considerable but variable excess of sulphur contained in solid solution. Thus upon cooling, unmixing would take place, giving rise to the lath-like inclusions of covellite. Where unmixing had proceeded far, or where the sulphur content was high, closely packed covellite laths would result. Less complete unmixing would give rise to the mottled blue-white chalcocite which contains microscopic and sub-microscopic covellite particles. In some cases unmixing may have been retarded or prevented, and then the sulphur (or covellite) would remain in solid solution, preventing the inversion of the chalcocite and giving rise to the widely distributed isometric chalcocite. In other cases the dissolved quantity of sulphur may have been small, and unmixing went to completion; or dissolved sulphur may have been lacking. Then normal orthorhombic chalcocite would result.

If all this be true, an adequate explanation would be provided to account for the occurrence of both isometric (commonest) and orthorhombic chalcocite, the intermingling of white and blue-white chalcocite, and the characteristic lath-like inclusions of

[19] *Op. cit.*

[20] It is not thought that all the covellite may have been formed by unmixing. Some of it, for example, the larger shapeless grains, was probably originally deposited directly as covellite.

covellite. Whether it is true, is the subject of further investigations which, it is hoped, may be published later.

SUMMARY.

1. Covellite and chalcocite form a solid solution when heated at moderate temperatures.

2. No change was noted at a temperature of 50° C., but at 75° C. a few per cent. of covellite in chalcocite became dissolved in three hours. At 100° to 120° C. solid solution took place in 1 to 2 hours.

3. Where the quantity of covellite reaches or exceeds 30 to 40 per cent. of the chalcocite present, solution is not complete; frayed remnants of covellite remain. Where covellite, on the other hand, is 90 to 95 per cent. of the chalcocite, only that covellite immediately surrounding the chalcocite disappears; the remainder of the covellite is unaffected. The reverse change, therefore, does not take place, *i.e.* chalcocite does not change to covellite at these low temperatures.

4. Complete solution takes place only with a relatively small proportion of covellite to chalcocite or with longer time.

5. Pure covellite is not affected by the same treatment that induces solid solution in mixtures of covellite and chalcocite. The change occurs only where chalcocite lies adjacent to covellite.

6. The lath-shaped outlines of former covellite persist in relief after solid solution occurs. Consequently, an increase in volume appears to have taken place in that part which was originally covellite.

7. Natural solid solutions of covellite (or sulphur) in chalcocite indicate their formation at elevated temperatures, hence they are of hypogene origin.

8. The change of covellite into chalcocite is considered to be one of solid solution and not by loss of sulphur from covellite.

9. The mechanism of the change is not yet understood.

10. Some unmixing of covellite from solid solution has taken place but consistent results have not been attained as yet.

11. The lath-shaped forms of covellite in chalcocite are con-

sidered to be due to unmixing and not to replacement, in the ordinary sense, of chalcocite by covellite.

12. The occurrence in the Kennecott ores of orthorhombic chalcocite, of large laths of covellite in chalcocite, of minute spicules of covellite in chalcocite, of "blue-white" chalcocite and of white isometric chalcocite, may be successive stages in the completeness of unmixing from solid solutions of covellite, or sulphur, in chalcocite.

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EDITORIAL

THE IMPORTANCE TO THE GEOLOGIST OF NON-METALLIC SPECIFICATIONS.

THE total value of the Non-Metallics in 1927, *exclusive* of mineral fuels, was $1,210,000,000, an amount very little less than that of all the metallic products.

Although the production value of the two is practically the same, their economic problems, so far as the consulting economic geologist is concerned, may be regarded as somewhat disproportionate, because those presented by the non-metallics are vastly greater owing to the widely varying uses of this class of materials.

If the geologist is called upon to make a commercial report on ore deposits, since their possible uses are well known, the report concerns itself chiefly with the origin, extent, and workability of the deposits.

But in the case of non-metallics, the consulting geologist is often required not only to determine the extent, form, and workability of the deposit, but also in most cases to suggest possible uses. This brings out the fact, if he does not already know it, that some materials of this group have most varied applications, which may be governed or determined by variations in the physical or chemical properties of the material itself. These the geologist should be familiar with, to deal with his problem intelligently.

A few examples may be given.

Clay may be used for a variety of clay products, such as common brick, paving brick, fire brick, china, or in paper manufacture. It is obvious that the same material may not serve all these purposes. What then are the distinguishing features of the material for each of these uses?

Diatomaceous earth may be employed as an insulating material,

filtering medium, abrasive, filler, or for structural material. Some grades serve best for one purpose and others for another. Why is this so?

Bentonite, a material now attracting much attention in the industries, may likewise have a range of applications, and the same is true of many other non-metallics.

Even sand, regarded by some as hardly worthy of notice, but of which $54,000,000 worth was produced in 1927, finds a place in a number of industries such as the making of glass, abrasives, structural materials, as a filler, and in the foundry. Any one sand cannot be used for all these purposes, and relatively small differences may sometimes be of great importance.

This means that in order to determine for what uses these materials are best adapted, we must, first, develop a knowledge of their physical and sometimes chemical properties; second, ascertain how these properties affect or determine their uses; and third, build up a series of specifications based on standard tests, which these several materials must meet, and with which the economic geologist engaged in non-metallic work should be familiar in order to judge a deposit intelligently.

It is true that in some cases the requirements or specifications for certain materials have already been worked out, but for others, this work is still to be done. To work these out satisfactorily may require considerable research, including the development of standard methods of testing. The problem may moreover call for coöperation between the technical man and more than one class of scientists.

To cite one case, reference may be made to molding sands, so widely used in the foundry.

Some eight years ago the American Foundrymen's Association sensed the need of accurate methods for testing the properties of molding sands, and the development of specifications for their selection. The problem was larger than it appeared to be at first sight but its importance was not under-estimated, and so both practical men and scientists including geologists, physicists, and chemists, were called in to help. The work brought out how little

is known regarding the properties of a common non-metallic product, but as a result of several years of research, there have been developed standard tests, which can be used to evaluate this raw material, and determine its uses for different purposes.

Similar opportunities are open in other fields of non-metallic geology and technology, and the entrance into them by the geologist, and technologist, working in coöperation, offers a chance to obtain interesting and valuable results. And incidentally it brings out the fact, already intimated, that the non-metallic geologist in consulting work cannot restrict himself to pure geology, but must also be more or less familiar with the technology of the materials he is studying.

H. RIES.

DISCUSSION AND INFORMAL COMMUNICATIONS

A NEW NATURAL INTERGROWTH OF BORNITE AND CHALCOCITE.

Sir: In a recent paper in this journal[1] the writer described a series of intergrowths of bornite and chalcocite which had been formed by slowly cooling solid solutions of the two minerals. The type of intergrowth shown in Figs. 9 and 10 was unknown in any natural ore at the time the pictures were published. It is

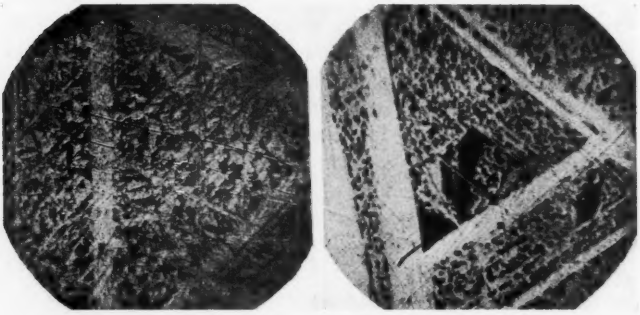

FIG. 1 (left). Specimen from Butte, Montana, containing about 65% chalcocite and 35% bornite, heated to form a solid solution, then cooled from 300° C. to 60° C. in 69 hours. Triangular pattern of chalcocite with bornite-chalcocite intergrowth inclosed. The inclosed intergrowth probably represents a eutectoid pattern. ×615.

FIG. 2 (right). Triangular laths of chalcocite enclosing intergrowth of bornite (dark) and chalcocite. Compare with Fig. 1. Specimen from drill hole at Mufulira, Northern Rhodesia. ×615.

[1] "Experiments Bearing on Bornite-Chalcocite Intergrowths," ECON. GEOL., vol. 23, pp. 381–397, 1928.

well shown by Fig. 10 of the original paper, reproduced here as Fig. 1.

Recently, through the courtesy of Dr. F. F. Grout, the writer examined a suite of ores submitted by Dr. F. A. Gray from explorations at Mufulira, Northern Rhodesia. A specimen from drill hole Number 2, at a depth of 437–444 feet showed copper sulphides disseminated in dolomite. Examination of a polished surface of one of the larger sulphide areas (about 4 mm. across) revealed chalcocite as laths arranged in triangles and enclosing a very intimate intergrowth of bornite and chalcocite. (See Fig. 2.) This natural intergrowth very strikingly resembles the intergrowth produced artificially as is shown by a comparison of Figs. 1 and 2. The analogy between the two textures is so close that it seems probable that they are of the same origin; that is, formed by the breakdown of a solid solution of the two minerals. The texture suggests eutectoid deposition with chalcocite in excess forming the laths and enclosing areas of chalcocite and bornite of the eutectoid composition. The artificial texture results from the breakdown of a solid solution at a temperature near 200° C.

It is especially interesting to discover the texture in a natural ore after it had been made artificially.

G. M. SCHWARTZ.

DEPARTMENT OF GEOLOGY,
UNIVERSITY OF MINNESOTA.

UPLAND DIAMOND DEPOSITS, DIAMANTINA DISTRICT, MINAS GERAES, BRAZIL.

Sir: The November, 1928, issue of ECONOMIC GEOLOGY published a paper by Mr. L. S. Thompson dealing with the geology of the important diamond district of Minas Geraes—a region carefully studied since 1822 by a number of scientists.

Unfortunately, the author persists in some errors that underly the work of geologists unfamiliar with Brazilian features.

The scientific investigation of this diamond-bearing area began with Henri Gorceix and Orville A. Derby. The latter published his studies in the *American Journal of Science*. His

thorough analyses of the subject were continued when he became the director of the Brazil Geological Survey. Later, other searchers, such as Euzebio de Oliveira, Djalma Guimarães, Luciano Jacques de Moraes, E. C. Harder, and R. T. Chamberlin, looked into the problem. As a consequence, a few definite points of Brazilian geology may be held as settled, and a few others admitted as a first approximation to reality.

No doubt, the question is extremely difficult and therefore the slightest confirmed progress ought to be carefully noted. For this reason, it is to be regretted that, instead of finding valuable suggestions in Mr. L. S. Thompson's paper, we are forced to defend the already definitely established points of the problem.

General Geology.—It is quite true that erosion has operated in this country since Silurian time; the Serra do Espinhaço (Derby, *Journal of Geology*, XV., pp. 394–401, 1907), since its uprising, between the Silurian and Devonian periods, has been eroded until the present day.

The Basement Complex.—What Brazilian geologists have called the "basement complex" or "Brazilian complex" is a system of rocks of pre-Algonkian age, including Archean representatives, numbering mica-schist, gneiss, granite, and limestone.

The rocks quoted by the author belong to the "Minas Series" (Algonkian): phyllites, quartzites (itacolomite), which, in fact, are "separated from the rocks immediately overlying it by a marked unconformity." But "the rocks immediately overlying" are not "the Caraça quartzite," since the name was precisely given by Harder and Chamberlin to the basal formation of the "Minas Series" (Algonkian), as L. S. Thompson refers it; it is a Cambrian sandstone, conglomeratic at its base—the Itacolomy Sandstone of Harder and Chamberlin.

The Caraça Quartzite.—The author has confused this formation with the metamorphic sandstone and the Cambrian quartzite, which, in fact, "covers the greater part of the area." "At, or very near, the base of the" metamorphic sandstone (not Caraça quartzite) "is a rather persistent bed of conglomerate." Here, however, there is more confusion regarding the fluvial and fluvioglacial formations of Sopa, Dattas, Serrinha, Bôa Vista, and the

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Cambrian conglomerate bed. Sopa and Guinda and similar deposits have local terrigeneous features, and date probably from post-Silurian days, whereas the Cambrian formation is a marine sediment.

It is well known that the "Caraça Quartzite" contains no diamonds, which are frequently to be found, even in paying quantities, in Cambrian and post-Silurian conglomerates. On the other hand, as intrusive diamond-bearing rocks in the Caraça Quartzite (S. João da Chapada) do not affect the Cambrian sandstone, data enough are given to fix the age of the diamonds in the State of Minas Geraes.

Between the Silurian and the Devonian, a phase of intense activity of granitic magmas occurred. From this period, no rocks intrusive into Cambrian beds are known to hold diamonds.

Authors who have tried to establish a parallel between the South African and the Brazilian diamond-geology have, as a whole, been led to gross mistakes.

This question has to be inquired into with absolute absence of preconceived ideas or theories; if the contrary is true, similar errors will constantly arise.

Igneous Rocks.—I cannot agree with the author's views on Bôa Vista, since in the possibly fluvio-glacial conglomerate the breccia has not yet been found. In fact the company actually working at Bôa Vista is developing its prospecting in order to discover this breccia.

As regards the cement of the S. João da Chapada breccia, I would strongly suggest that the author peruse the work of Orville A. Derby.[1] The abundant analyses presented in these papers, some of them very complete, show that this cement is "sericite," containing 3.7 per cent. of magnesia, at the utmost.

Origin of the Diamonds.—As a consequence of the mistakes pointed out in the preceding lines, the author was led to assert that the diamonds were formed in the Caraça Quartzite as a detrital mineral. As this formation is Algonkian in age (Harder and Chamberlin, Euzebio de Oliveira) the gems should have been

[1] "On Certain Schists of the Gold and Diamond Regions of Eastern Minas Geraes, Brazil," *Amer. Jour. Sci.*, X., 207–216, 1900; Bulletin 24, Brazilian Geol. Survey.

derived from pre-Algonkian rocks or the crystalline complex. Nevertheless, on page 716 we find: "The age, then, is probably not earlier than late Paleozoic, and possibly Mesozoic."

Diamonds as detrital constituents are formed in the Cambrian conglomerate ("Lavras Series" of Brazilian geologists) and as an accessory element in the eruptive breccia crossing the Algonkian formations.

According to analytical and petrographical studies, made by Gorceix, Derby, and the present writer, it is impossible to avoid the necessity of formulating a different hypothesis as to the origin of diamonds in Brazil, and the physico-chemical conditions of formation.

Among the buyers of gems in Diamantina, the occurrence of quartz inclusions in diamonds is known; in 1923, R. J. Colony published a note[2] on the intergrowth of quartz and diamond in a Brazilian specimen.

If it be borne in mind that the eruptive breccia holds only accessory minerals, commonly found in acid or neutral rocks (tourmaline, zirconite, magnetite, monazite, hematite, rutile), and is composed almost entirely of sericite and quartz, it will seem much more logical to admit that it came from an original acid or neutral rock than from an ultra-basic one.

In this last hypothesis, how might the absence of chromite be accounted for, since it is known to be so resistant to intense metamorphic agencies?

I cannot see sufficient evidence to establish a parallel between the diamond deposits of Brazil and those of South Africa.

I feel deeply impressed, on the other hand, that the more Kimberley is studied, the less clear is our knowledge of the origin of the diamond.

In purely scientific researches, geologists ought always to be on guard against the commonly heard saying, "I have seen this in such places." Every occurrence ought to be investigated with its own characteristics and the data it offers.

DJALMA GUIMARÃES.

BRAZIL GEOLOGICAL SURVEY,
RIO DE JANEIRO, BRAZIL.

[2] *Amer. Jour. of Sci.*, (5) V., p. 400, 1923.

REVIEWS

The Evolution of the Igneous Rocks. By N. L. Bowen. Pp. x + 331, Princeton University Press, 1928. Price $5.00.

Bowen's contributions to petrogenesis during the last fifteen years have been so outstanding that every petrographer will read with eager interest his latest book. This book is in a large measure a restatement in a more connected and concise form of his former papers, but contains some new evidence and arguments and some further details. Bowen's thesis is that igneous rocks are all derived from a basaltic magma and that the variations in composition are brought about chiefly by crystallization and separation of liquid from crystals, in small part by the settling of crystals into a liquid. His conclusions are based largely on the evidence furnished by the equilibrium diagrams of artificial systems and this point of view has led to some of the most important contributions to petrology. Yet the critical reader should consider carefully the amount of extrapolation involved in this line of reasoning. No system of more than three components has been completely worked out, yet rock systems have at least eight important constituents. FeO, Fe_2O_3, H_2O, and many of the minor constituents are not represented on any of the equilibrium diagrams. In the equilibrium diagrams, silica comes out as tridymite; orthopyroxene is not represented but only the solid solution series clinoenstatite-diopside. Biotite and hornblende do not appear.

After discussing the equilibrium diagram for a simple two-component system with limited miscibility and Greig's experiments on immiscibility in silicate melts, Bowen concludes that immiscibility in silicate magmas is of no importance. Should the possibility of limited miscibility in some water-rich magmas near the temperature of final consolidation be denied?

He gives an excellent discussion with equilibrium diagrams of the crystallization of a set of two- and three-component systems well selected for the petrologist. He discusses the reaction principle and reaction series much as in his former papers. His conclusion that the diabase structure is formed by the simultaneous crystallization of plagioclase and pyroxene will not be accepted as proven by some petrologists.

In answer to Fenner, Bowen concludes that the variation diagrams of the hornblendic series of Lassen Peak, the pyroxenic series of Mull, and the rocks of Katmai are such as would be expected from crystal differentiation. He also concludes that the residual liquids are not en-

riched in iron, as might be concluded from Vogt's studies. The hornblendic series is richer in Al_2O_3, CaO, and MgO, and poorer in Fe_2O_3, FeO, and K_2O. Bowen considers only the Al_2O_3 but the MgO and iron may be equally important, especially as hornblende when resorbed yields pyroxene and magnetite. The liquid is enriched in Al_2O_3 by slow cooling with reaction between the plagioclase crystals and the liquid, thus enriching the liquid in anorthite. On pages 99 and 101 in the system Ab-An-Or the opposite effect is shown by slow cooling.

In many places Bowen emphasizes the necessity of carefully distinguishing between rocks from the liquid line of descent from those formed partly by crystal accumulation. These latter have no aphanitic or glassy forms but always carry phenocrysts.

From a plot of the chemical analyses of the perlites and pitchstones, and a second of the obsidians, he shows that the high silica members of the former are richer in K_2O and are the equivalents of the pegmatites and silica-rich pegmatites. However, many American pegmatites have a much higher proportion of soda. There are no glassy equivalents of the granites very rich in SiO_2 nor of those with high K_2O and low Na_2O or high Na_2O and low K_2O, and such rocks are believed never to have been completely liquid.

An excellent study of the Mull rocks and of other basalts leads to the conclusion that no aphanites have a normative plagioclase richer in anorthite than $AbAn_2$ and that basalts with a higher anorthite content were never completely liquid.

A field and laboratory study of the picrites and peridotites of Skye led to the conclusion that a basaltic intrusion preceded and prepared the way for the picrites and peridotites which were largely crystalline when intruded.

The discussion of the effect of a magma on inclusions is excellent, as Bowen's contributions to this subject are outstanding. Solution of a silicate is accompanied by a large absorption of heat and, as there is little excess heat in a magma, little material can be dissolved in a magma without precipitating a corresponding amount of something else. Limestone reacted on by a magma should increase the magnetite and olivine and make the pyroxene richer in diopside and the plagioclase richer in anorthite. Kaolin should make the plagioclase richer in anorthite and the pyroxene richer in MgO. In most cases reaction on inclusions, changes only the proportion of the constituents of the rock, but in some it causes the crystallization of new phases.

Bowen discusses in detail the emery deposits near Peekskill, N. Y., and concludes that they are unquestionably due to reaction of the gabbro magma on aluminous sediments. His evidence is chiefly the analogy

between the emery deposits and the artificial systems. The analogy is far from perfect and is probably not so close as the analogy between the Peekskill emery deposits and those of Virginia, which cannot be explained as due to reaction since the intrusive is a granodiorite but are believed to have been formed by hydrothermal contact metamorphism.

Bowen's discussion of the origin of the potash-rich rocks is highly hypothetical. He draws an equilibrium diagram for the feldspar (Ab-An-Or) showing a reaction relation between orthoclase and lime-rich plagioclase. His evidence is the presence of rims of orthoclase about calcic plagioclase but he ignores the rims of sodic plagioclase about potash feldspar in the Rapikive granites and elsewhere. If crystallization takes place according to his diagram with reaction, the liquid is enriched in K_2O and if it reaches the orthoclase-plagioclase boundary curve in the range where orthoclase has a reaction relation to plagioclase and reaction is later prevented, the liquid will continue to be enriched in orthoclase. This is consistent with the fact that most potash-rich rocks have a calcic plagioclase.

The discussion of the origin of the alkali rocks is, perhaps, the least convincing. In the hydrous granitic magma formed by progressive crystallization and separation of the liquid from an original basaltic magma, the albite breaks down to form nepheline and silica. Quartz crystallizes, leaving a mass of quartz crystals and a little interstitial liquid with the composition of a phonolite. The failure to find quartz crystals in phonolites is due to the fact that such a mixture cannot be injected into small fractures and hence is never chilled (?). The pegmatites are the late differentiates only of potash-rich rocks.

Syenites may be formed as a late differentiate in place of granite by preventing the precipitation of olivine in excess, either by rapid cooling or in a magma whose pyroxene is so rich in diopside (over 80 per cent.) that the reaction relation between olivine and pyroxene does not exist. Such rocks should have a pyroxene rich in diopside.

The anorthite-leucite-silica diagram shows a reaction relation between orthoclase and leucite and this is true in a more complex system unless the solution is too rich in either Na_2O or SiO_2. When a basaltic liquid crystallizes slowly with reaction, the liquid phase may reach the orthoclase field where leucite crystallizes from a lime-rich liquid but without reaction. The orthoclase field is reached when the liquid is too high in Na_2O for the formation of leucite. Hence leucite is found chiefly in highly calcic rocks. Leucite may settle from the rhyolitic liquid although its density cannot be much greater than that of the liquid. If leucite crystallizes and remains in the liquid it may be reacted on to form pseudo-leucite which is a mixture of orthoclase and nepheline. Some nepheline rocks may be formed in this way.

Bowen discusses the origin of the alnoites much as in his former paper. The magma crystallized until olivine and augite made up nearly the whole of the mass. Reaction between the liquid and crystals replaced nearly half the crystals by biotite, monticellite, melilite, and perofskite.

The chapter on volatile constituents is excellent and should be of especial importance to economic geologists. It gives equilibrium and pressure-temperature diagrams of several salt systems with water and discusses the second boiling point. It shows with diagrams the effect of critical temperature on solutions and concludes that if critical phenomenon occurs in magmas at all, it must be only in the highly aqueous residues and probably not then. There are no vesicules in deep seated rocks, and the only means of moving the gases is by diffusion. The volatiles probably escape during the later stages of crystallization.

Bowen favors as a source for the primary basalt, the selective fusion on release of pressure of peridotite and movement of the liquid part. Would this yield the uniform liquid that seems required?

This book is an outstanding contribution and should be read, pondered and re-read, for on it much of our progress in the study of the igneous rocks will be built. However, since progress is much delayed by overconfidence in our knowledge, the reader is warned that Bowen's great reputation, his vigorous presentation, and the positiveness of geophysical arguments may mislead one into concluding that the whole matter is unquestionably settled.

Progress may be expected especially from the study of the rocks themselves in the field and laboratory, based on Bowen's methods and conclusions.

ESPER S. LARSEN.

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Analytical Principles of the Production of Oil, Gas, and Water from Wells. By STANLEY C. HEROLD. Pp. 659, figs. 209, 10 appendices, index. Stanford University Press, Cal., 1928. Price, $7.50.

This formidable-looking volume seems, because of its thorough mathematical treatment of the subject, to terrify some readers. It does appear to be largely an involved mathematical discussion of the subject. Professor Tolman points out in the preface that the subject is susceptible only to mathematical treatment but that the mathematics is really quite simple. He further points out that with an understanding of the three "controls," namely, Hydraulic control, Volumetric control, and Capillary control, the subject matter can then be followed.

The treatise gives the fundamental laws governing fluid delivery from wells, and shows that measurements can be made to furnish the data necessary for the solution of the various equations discussed, and that the control under which a well is producing can be easily determined. It is a pioneer work which should prove to be the foundation for further knowledge of the control of wells.

Fortunately for the reader, Mr. Herold's rather involved and abstruse reasoning has been abstracted in a lucid nine-page summary by Mr. Ernest K. Parks, Petroleum Engineer of the Standard Oil Company of California. A reading of this summary enables one to delve into the text to obtain the information he may desire. Mr. Parks concludes by saying:

"One of the causes of overproduction is the fear that neighboring wells will drain the property if it is not developed rapidly. This fear is well founded in reservoirs of Hydraulic and of Volumetric control. In these we need co-operation among the various operators. On the other hand, this fear is absolutely unfounded in reservoirs of Capillary control. Co-operation is unnecessary; single offsets to the adjoining wells are entirely sufficient to prevent drainage; the remaining oil within the interior of the property will rest untouched until the end of time. By means of the principles brought forth in this treatise we shall see the stabilization of the industry. We shall obtain the greatest amount of oil at the least cost only so rapidly as we need it for the market.

This is not a book that one can peruse; it must be studied. But whoever wishes to solve the problems of the production of fluids from wells must turn to it.

ALAN BATEMAN.

Diamond: A Descriptive Treatise. By J. R. SUTTON. Pp. xii + 118, pl. 35, figs. 3. Thos. Murby & Co., London, 1928. Price, $4.00.

As its title indicates, this is a description of diamond as found mainly in South Africa. It pictures in great detail diamond crystals, the markings on their faces, intergrowths, etched figures, etc., and discusses briefly their physical properties. The author contradicts many of the statements that have been made by earlier students of diamonds, since "the amount of misstatement even on matters of simple observation is extraordinary," but, so far as the reader can discover, does not offer any clearly expressed substitutes. He declares that no theory that has been proposed to explain the origin of diamonds has been proven correct. The supposed synthetic diamonds formed under conditions of great pressure and high temperature he suspects are "more likely a kind of carborundum." The diamond in the rocks in South Africa is not an early separation from the magma, but it "belongs at least to the youngest generation of primary minerals,"

and crystallized in marginal cavities in eclogite nodules. The author believes, with Friedel, that before crystallization the material composing the crystals was in a plastic condition, that the strains exhibited in crystals may be due to contraction, and that the twinning was produced by "hemitropic rotation, not always complete, of one part xx on the other part, and under pressure." No satisfactory evidence is given for any of these views. They are merely inferences based mainly on interpretations of the shapes of crystals and crystallized masses. No explanation of the origin of diamonds is offered, although there is a chapter headed "The Genesis of Diamond."

The book is abundantly illustrated with photographs of individual diamond crystals and groups of crystals. It contains an excellent account of the forms in which diamonds occur, and the characteristics of their imperfections, but otherwise has little material of general interest to the student of diamonds.

W. S. BAYLEY.

The Last Glaciation. By ERNST ANTEVS. Pp. 292; figs. 30; pl. 9. American Geographical Society Research Series No. 17, 1928.

In this book there is presented a great accumulation of data concerning the last glaciation, special attention being given to the glaciated area of eastern North America. Interesting problems such as climate during glaciation, rate of ice recession, and contemporaneity of glaciation in various parts of the world are considered. New varve measurements and correlations are given in an appended series of nine plates. An extensive list of references is given. Altogether, it is a valuable assemblage of detailed information on a very live subject. The make-up is a credit to the American Geographical Society.

E. S. SILK.

Geology of the Country around Lonely Mine, Bubi District, Southern Rhodesia. By A. M. MACGREGOR. Pp. 96, pl. 7, maps 3. So. Rhod. Geol. Survey Bull. 11, Salisbury, 1928. (Feb., 1929.)

Another of the excellent bulletins being gotten out by the progressive Geological Survey of Southern Rhodesia under H. B. Maufe. Few people realize that the Lonely Mine is more than 4,000 feet deep and has produced over $21,000,000 in gold from a quartz fault fissure. Its temperature gradient from 1,000 to 3,675 feet is 1° F. in 191 feet. The ore is partially oxidized to a depth of 3,000 feet.

BOOKS RECEIVED

Platinum and Black Sand in Washington. By J. T. PARDEE. 15 pp. U. S. Geol. Surv. Bull. 805–A, 1929 (Feb.).
Platinum and gold of the black sands; history and geology.

Preliminary Report on the Sheenjek River District, Alaska. By J. B. MERTIE, JR. 23 pp. U. S. Geol. Surv. Bull. 797–C, 1928 (Feb., 1929).
Geography and geology of a large area north of Fort Yukon.

Mineral Industry of Alaska in 1927. By PHILIP S. SMITH. 85 pp. U. S. Geol. Surv. Bull. 810–A, 1929 (Feb.).
Production of the different metals and new developments.

Glaciation et Morphologie du Bassin de la Vistule Moyenne. By S. LENCEWICZ. Pp. 194, figs. 27, pl. 11. In Polish, with resumé (25 pp.) in French. Geol. Surv. of Poland, vol. II, livr. 2, 1927 (Jan., 1929).
A comprehensive discussion.

Subsidence and Ground Movement in the Copper and Iron Mines of the Upper Peninsula, Michigan. By W. R. CRANE. Pp. 66, illus. 49. U. S. Bur. of Mines Bull. 295, 1929 (Mar.) Price, 40 cts.
Theoretical consideration and specific illustrations of subsidence.

West Virginia Academy of Science, Proceedings, Vol. 2, 1928. 200 pp. West. Va. Univ. Bull. Ser. 29, No. 1.
A creditable publication; includes several good geological papers.

The Rock River Country of Northern Illinois. By D. ROLFE. 58 pp. Illinois Geol. Surv. Educat. Ser. No. 2, Urbana, 1929.
Excellent popular educational pamphlet.

Contributions to Canadian Mineralogy, 1928. Pp. 28, illus. The Crystal Structure of Sperrylite, by G. AMINOFF and A. L. PARSONS; A New Telluride Occurrence in Quebec, by ELLIS THOMSON; Pleochroic Haloes in Biotite, by D. E. KERR-LAWSON. Univ. of Toronto, Geol. Series 27, 1928 (Mar., 1929).

The Hudson Bay Region. By F. H. KITTO. Pp. 50, illus. Natural Resources Intell. Serv., Ottawa, 1929 (April).
History, climate, resources, references.

Coal Stripping Possibilities in Saline and Gallatin Counties near Equality, Illinois. By L. G. HENBEST. 26 pp., maps. Ill. State Geol. Survey Mining Ser. Bull. 32. Urbana, 1929 (Mar.).

Fluorspar in New Mexico. By W. D. JOHNSTON, JR. Pp. 128, figs. 40. New Mexico Bur. of Mines Bull. 4, Socorro, 1928 (Mar., 1929).
Mineralogy, geology, distribution.

SCIENTIFIC NOTES AND NEWS

Dr. H. Schneiderhöhn, of the University of Freiburg, is conducting a party through some of the mining regions of Southwest Africa, and will later attend the International Geologic Congress at Pretoria.

George Otis Smith, Director of the U. S. Geological Survey, lately made a trip to California in the interests of the conservation of petroleum resources.

C. A. Heiland, professor of geophysics at the Colorado School of Mines, is investigating geophysical methods in European institutions. He will return to Golden in September.

E. L. Bruce, professor of mineralogy at Queen's University since 1920, has been appointed first Miller Memorial Professor of Research Geology at the University. This new chair was founded in memory of the late Dr. Miller.

E. F. Burchard is taking two months' leave of absence from the U. S. Geological Survey which he will spend in South America in commercial work.

Carlton D. Hulin, of the University of California, is engaged in geological work for the U. S. Smelting, Refining & Mining Co., at the Sunnyside Mine in southwestern Colorado.

H. A. Brouwer, professor of geology at the Technical University at Delft, Holland, has been appointed director of the new Geological Institute at the University of Amsterdam, where he will occupy the chair of general geology and petrology. He is now in the East Indies and will act as delegate to the Fourth Pacific Science Congress.

C. K. Leith and W. J. Mead of the University of Wisconsin conducted a student party through the pre-Cambrian mining districts of Minnesota and Michigan last month.

J. L. Gillson, of the Mass. Institute of Technology, is taking a year's leave of absence and will act as associate professor of economic geology at Northwestern University, Evanston, Ill.

J. J. Sederholm, director of the Geological Survey of Finland, received the honorary degree of Doctor of Laws at Queen's University, Kingston, Canada, recently, and delivered the Miller Memorial lecture course there during January and February.

F. L. Ransome, professor of economic geology at the California Institute of Technology, is attending the International Geological Congress as a delegate from the National Academy of Sciences, National Research Council, and other institutions, and will spend some time in Northern Rhodesia after the Congress session.

Clinton H. Crane, president of St. Joseph Lead Company, delivered the commencement address at the Colorado School of Mines, and was

awarded the honorary degree of Doctor of Science by that institution.

J. E. Hawley has been appointed head of the department of mineralogy at Queens University, Kingston, Canada, succeeding E. L. Bruce.

F. A. Kerr, of the Canada Geological Survey, is now in Honolulu recuperating from overwork.

Harold S. Munroe succeeds C. B. Kingston, resigned, as consulting engineer for the Anglo-American Corporation in Northern Rhodesia.

A. P. Coleman and E. S. Moore are in the Sudbury district, Ontario, inspecting the Gordon Lake Holdings property at the southwest end of the Sudbury Basin.

Frederick W. Clapp, 50 Church Street, New York, who has been visiting oil fields in Egypt and other points in the Near East, has rejoined his family in Paris.

Guy N. Bjorge, consulting mining geologist of San Francisco, recently spent several months in Brazil, in professional work for the St. John de Rey Mining Co.

F. E. Calkins has been making a geologic survey of the Santa Rita district, New Mexico, where the American Smelting and Refining Co. is undertaking the development of a large group of claims.

Foster S. Naething, consulting mining engineer, formerly of St. Louis, has removed his offices to 74 Trinity Place, New York.

The Physical Exploration Corporation has established an office in Vancouver, B. C., under the management of M. D. Harbaugh, at 849 Georgia St.

D. F. Higgins, of Northwestern University, is to be professor of geology at Lincoln Memorial University, Harrogate, Tenn., the coming year.

The first number of the Annotated Bibliography of Economic Geology will be off the press this month. Those wishing to subscribe should send subscription ($5.00 per year) to W. S. Bayley, University of Illinois, Urbana, Ill.

The University of Cologne has arranged a geological excursion from July 21 to August 4, conducted by Professor Philipp, director of the department of Geology and Mineralogy, which will include the geologically interesting and scenic parts of the Rhineland and the large centers of the Rhenish mining industry. Total expense including board and lodging will be about 200 marks. Details can be obtained from the Geologisch-Mineralogische Institut, Cologne, Severinswall 38.

Mrs. W. S. Bayley, wife of the Business Manager of this Journal, died May 10 after a long illness.